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# AQUEOUS SOLUTION AND THE PHASE DIAGRAM

*by*

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# AQUEOUS SOLUTION AND THE PHASE DIAGRAM

## CHAPTER I

### INTRODUCTION

This book, as indicated in its title, deals with phase diagrams rather than with the phase rule. It is also limited to aqueous solutions. For a more comprehensive treatment of phase theory and of heterogeneous equilibria in general, the reader is referred to other works such as *The Phase Rule and its Applications*, by Alexander Findlay and A. N. Campbell (8th edition, 1938), *The Principles of the Phase Theory*, by Douglas A. Clibbens (1920), *The Phase Rule and the Study of Heterogeneous Equilibria*, by A. C. D. Rivett (1923), and *The Phase Rule and Phase Reactions Theoretical and Practical*, by Sydney T. Bowden (1938). For other specialized aspects of the phase rule there are *Equilibria in Saturated Salt Solutions*, by W. C. Blasdale (1927), *The Industrial Development of Searles Lake Brines with Equilibrium Data*, by J. E. Teeple (1929), *States of Aggregation*, by G. Tammann, translated by R. F. Mehl (1925), and *A Textbook of Metallography*, by G. Tammann, translated from third German edition by R. S. Dean and L. G. Swenson (1925). An introduction to the phase theory is given by J. E. Wynfield Rhodes in *Phase Rule Studies* (1933).

Among these books there was the need for a more practical and elementary explanation of the use of phase diagrams. It is hoped that this book may serve first as an introduction and then as a laboratory manual or desk companion for those workers who wish to apply this method for the solution of problems of heterogeneous equilibria. In aqueous solutions such problems include the separation of pure chemicals from mixtures, the preparation of double compounds and hydrates, the cyclic re-use of mother liquors, the right amount of evaporation or dilution required to give the best economic result consistent with purity of product and the effect of the addition of other salts, or the accumulation of impurities. The progress of such operations can be followed quantitatively and optimum conditions can be determined.

There are many practical uses of phase diagrams which may be applied without much advanced knowledge of the phase theory. If this were more generally realized we believe that chemical industry would benefit by the much greater application of a simple method of dealing with the types of problem indicated above. For this reason the explanation of the phase rule has been relegated to the last chapter and the practical construction and interpretation of diagrams has been presented so that they can be used simply from a knowledge of geometry and arithmetic. The chemist performs a series of ordered experiments to prepare his diagram and he can then predict the results of endless experiments with pencil and straight edge until he arrives at the one set of conditions which give the desired result. At the same time it must be admitted that an understanding of phase theory in general adds considerably to the interest in the subject and just sufficient theory has been introduced to provide this interest.

With regard to actual diagrams reproduced, we have in every case given the data as well as the diagram, so that the reader may plot his own figure. This is the best way to understand phase diagrams. Further, we believe that practical application creates an

understanding more quickly than does mere theorizing and so, in explaining various points, we have usually begun at once with actual examples avoiding, as far as possible, preliminary explanations with hypothetical cases. Thus real chemicals have been used rather than the imaginary *ABC* or *XYZ*, except for the reciprocal salt pair of Tables 22, 23, 24 and for the five-component diagram of Fig. 40.

The Phase Rule was deduced from thermodynamic considerations by J. Willard Gibbs, Professor of Mathematical Physics at Yale University, and published in 1876, *Trans. Conn. Acad.*, 1876, 3, 152. See also *Collected Works* of J. W. Gibbs, Vol. I, published in 1928 by Longmans. This rule gave a relationship between phases, degrees of freedom and independent components. It may be expressed simply as

$$P + F = C + 2$$

where  $P$  = number of phases,  $F$  = number of degrees of freedom, and  $C$  = number of independent components.

Gibbs's work was unnoticed except by a few and no attempt was made to use his important generalization until it was disclosed, in a somewhat new form, by Bakhuis Roozeboom in 1887 when, at the suggestion of van der Waals, he applied it in his researches and showed the fundamental importance of the principle as a guide to the behaviour of heterogeneous systems. (See B. Roozeboom's book, *Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*, which first appeared in 1904 and was continued, after Roozeboom's death in 1907, by Meyerhoffer and Schreinemakers.)

It was Roozeboom who made the theory of Gibbs generally accessible, but it was the work of J. H. van't Hoff which inspired other workers, not only of his own time, but right up to the present day. van't Hoff was unaware of the work of Gibbs when he was studying chemical equilibria in 1881 and when he enunciated his own laws which, in some respects, coincided with Gibbs's phase rule.

By 1896 van't Hoff had carried out researches on the formation of double salts and had started his classical investigation on the salt beds of Stassfurt, so that it was van't Hoff and his co-workers who provided the first important example of the practical application of Gibbs's work (see van't Hoff's *Ozeanische Salzablagerungen*).

We are indebted to America for the phase rule, but it is largely due to the energies and imagination of a small group of Dutchmen that this branch of physical chemistry has been developed.

In more recent years the tendency to make use of the phase rule in industry has increased and a great mass of data has been collected in both America and Europe. Though less attention has been paid to the subject in this country, as indicated by the fewer publications in British journals, there have been numerous researches by Bassett, Findlay, Rivett and others, but more notably those of Freeth and his co-workers. In 1915 the researches of Freeth made it possible to obtain ammonium nitrate from Chile saltpetre when, to quote the words of Professor Donnan, he "took the phase rule of Gibbs into the very cannon's mouth."

The enunciation of the rule was only part of the story and the fuller use has, to a large extent, been based on the development of improved graphical methods for the representation of the equilibrium. The use of Cartesian co-ordinates for plotting the simple solubility curve for one salt and water was only the beginning; composition was usually the abscissa and temperature the ordinate, although some books reverse this.

In 1827 Mobius had introduced his triangular or trilinear co-ordinates whereby points

dependent upon three variables could be plotted provided the third variable was dependent upon the other two in the sense that the sum of the three was equal to unity, or to some other standard. (*An Elementary Treatise on Trilinear Co-ordinates*, N. M. Ferrers, 1861; *Trilinear Co-ordinates and Other Methods of Modern Analytical Geometry of Two Dimensions*, W. A. Whitworth, 1866.) Willard Gibbs used these trilinear co-ordinates<sup>1</sup> for three-component systems making the height of the equilateral triangle the standard, e.g. unity or one hundred (*Trans. Conn. Acad.*, 1876, 3, 176). Roozeboom made the side of the triangle his standard (*Z. physik. Chem.*, 1894, 15, 145). Both amount to the same thing but different measuring scales are required. In this book, as in other recent works, we have rather combined the two, expressing position within the triangle more in terms of the lattice and using an imaginary parallel rule. Such a method is more readily applied to triangles of irregular shape. Printed graph paper for plotting on trilinear co-ordinates can be purchased as *triple co-ordinate* paper and we have used this term.

With the introduction of more components the full representation of phase diagrams necessitated more dimensions, even beyond three, and various devices have been introduced to eliminate one or more of the variables. Pressure was first eliminated for aqueous solutions by considering the systems, not at uniform pressure, but at such pressures that there was no vapour phase. Thus the diagrams are not isobars but represent "condensed" systems. Atmospheric pressure usually fulfils this condition for practical purposes.

Temperature was then eliminated, in this case, usually by having a fixed temperature, that is the diagram represents an isotherm. With the exception of the diagrams in Chapter II, representing binary systems, all the diagrams in this book are isotherms. Polythermal diagrams can be prepared for systems representing water and two or even more salts. Such *polytherms* are figures in space and are generally shown as isometric perspective projections of such three-dimensional figures. Such diagrams have a limited use and in this book, for simplicity and easy application, we have used only isotherms and have superimposed one or more isotherms in one plane when polythermal reactions are being considered. The reader may imagine that the upper part of Fig. 35 is a polytherm, but it also is simply the projection of two isotherms on to a plane; a polytherm would show curvature as the temperature was *gradually* changed whereas Fig. 35 merely shows the results at two specific temperatures.

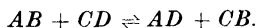
Water was eliminated by the device of projecting from the point representing water. This was introduced by Ernst Jänecke, "Über eine neue Darstellungsform der van't Hoff'schen Untersuchung über ozeanische Salzablagerungen," *Z. anorg. Chem.*, 1906, 51, 132; 1907, 52, 358, and 1907, 53, 319. His presentation was not good and did not receive the merit it deserved; in fact, fifteen years later, Henry Le Chatelier, in *Compt. rend.*, 1921, 172, 345,<sup>2</sup> put it forward as a new idea. Rivett in *The Phase Rule*, page 171, states that "the method offers no particular advantage over the pyramidal" and he would prefer the latter to be adopted generally. We do not agree, as indicated in Chapter X. The pyramidal method is fully explained in Chapter IX, but this is merely to ensure a full and easy understanding of the later chapters on Jänecke's projection. The reader should not be tempted to omit Chapter IX.

Jänecke introduced several other methods of projection, as, for example, the projection of a triangular prism on to one of the rectangular sides from one edge, the lines of projection being parallel to the triangular ends and radiating from points along the edge.

<sup>1</sup> Gibbs's explanation is by no means clear and credit should go to Roozeboom for popularizing the method.

<sup>2</sup> Jänecke's reply, *Chem. Ztg.*, 1922, 46, 361.

The square-based regular pyramid was introduced by Löwenherz (*Z. physik. Chem.*, 1894, **13**, 459) for plotting reciprocal salt pairs, that is the system in which double decomposition may take place of the type :



It is of interest to note that van't Hoff introduced the sign  $\rightleftharpoons$  to represent mobile equilibrium.

No attempt has been made in this book to cover all the many different methods of plotting, projecting and using phase diagrams. The limited number of methods given has been based on practical experience over a large number of years during which time many published methods have been tried, modified and, we trust, improved and extended. This especially applies to the quaternary and quinary systems.

A phase reaction is a change in the number of phases or in their composition, a phase being a homogeneous part of the heterogeneous mixture. Interest in phase reactions centres in the fact that the change from homogeneous to heterogeneous mixtures gives a means of separating chemical substances, with or without chemical reaction. The change from heterogeneous to homogeneous gives a means of purifying the mixture from extraneous matter as in the filtration of dirt from a salt solution.

There are a number of terms used in any study of phase equilibria and these will now be explained, although the preceding has already had to make use of many of them. Some of these definitions are repeated in Chapter XIII in order to make that chapter complete in itself.

**A system** is a mixture of substances limited to contain only those substances which form its components and in which temperature and pressure may be altered as desired. The system may be specific, that is a particular mixture of the substances, or it may be general, that is it may refer to any mixture of the substances. In choosing the method of diagrammatic representation, the general study of the system will require the boundaries of the diagram, whether on a plane or in space, to be the limits of the system. Thus the system sodium chloride and water will have the limits to represent all sodium chloride and no water at one edge and all water and no sodium chloride at the other. It must not include mixtures of sodium chloride and alcohol, since the introduction of alcohol brings in another system. On the other hand, every system can be regarded as being limitless in the sense that it is always a small part of a larger system. In this sense the system sodium chloride and water would form part of the larger system sodium chloride, potassium chloride and water, but in that case the larger system would also include two others : potassium chloride and water ; sodium chloride and potassium chloride. This idea will be especially noted in studying the quinary system, Chapter XII.

In this book, where the term system would be used to specify a particular mixture, we have used the term **complex**.

The substances comprising the system, when they are independent, are called **components**. A component may be a chemical element or a compound, but the Phase Rule is only concerned with the *number* of components and not with their composition. Thus the number of components is the smallest number of chemical entities which can represent the system under the conditions being studied. Thus for a condensed system calcium carbonate is one component, but for a system at high temperature and with a possible gaseous phase it is a system of two components, calcium oxide and carbon dioxide. For the study of phase diagrams the number of components is of less interest than a knowledge



of all the chemical compounds which can exist within the system. Thus in the system of two components, sodium sulphate and water, we must know that there are at least three possible chemical substances, sodium sulphate, sodium sulphate hexahydrate (Glauber's salt) and water. The number of components is only required when one wishes to check results obtained from the diagram with the Phase Rule.

One-component systems are described as *unary*, two- as *binary*, three- as *ternary*, four- as *quaternary*, five- as *quinary*, and so on.

A **phase** is a homogeneous part of a mixture. The whole mixture may be homogeneous as in the case of an unsaturated solution or it may be a mixture of different physical states either of the same or of different chemical entities. Phases can be separated from one another by physical or mechanical means, in theory at least, even though this may not be always practicable. For example, a mixture of two kinds of crystals may be apparently inseparable, but the microscope will show the separation. Since gases are infinitely miscible the gaseous part of any system is always only one phase. Liquids form more than one phase when they are not miscible; for example, benzene and water. In aqueous salt solutions it is rare to have more than one liquid phase and so in this book discussion has been limited to cases where the liquid constitutes only one phase. Solids form as many phases as there are chemical substances present in the solid state. The exception is where solid solution or "mixed crystals" are formed. This book does not include such cases except for the brief reference at the end of Chapter VII. van't Hoff introduced the idea of solid solution—the expression "mixed crystals" is unfortunate as it gives the wrong impression.

A *phase diagram* is a graphical representation in two or three dimensions of the lines or surfaces of equilibrium between the phases in a system. Thus the lines and curves, planes and curved surfaces on the phase diagram indicate that a mixture (complex) on one side of the line or surface has a different set of phases from a mixture just on the other side. They may both have the same number of phases or not, but if they have the same number then their composition will be different.

Whereas the Phase Rule is only concerned with the number of phases and not their composition nor their relative proportions, the phase diagram enables both to be determined. Empirical data have to be obtained in order to be able to plot the diagram; the interpretation of the diagram enables one then to predict the course of a reaction with only a limited number of determinations.

A **degree of freedom** or of variability is a possible choice of conditions for the system which can be made without altering the number of phases. There are three kinds: pressure, temperature and composition. Pressure has been excluded from the discussions in this book and all aqueous solutions are assumed to be condensed. Temperature is a very important selection to be made. By composition is meant the composition of any of the phases and, for studies on aqueous mixtures, it is usually the composition of the solution which is of interest and which is taken. It does not mean the composition of the mixture (complex)—this is important as by false reasoning the ability to change the composition of the complex may be mistaken for a degree of freedom although the composition of the phases remains unaltered. For example, if water is added to a mixture of salt solution and solid salt (temperature kept constant), some salt will dissolve, but so long as insufficient water is added there will still remain a mixture of salt solution (saturated at that temperature, and therefore of fixed composition) and solid salt (though less in proportion). The addition of the water does not constitute the selection of a degree of freedom: this statement must

have added to it the words, *within limits*. Obviously if sufficient water is added to dissolve all the solid salt, then the solution will become weaker and a selection of a degree of freedom has been made, the composition of the liquid phase.

A system with no degrees of freedom is described as *invariant*, with one degree as *univariant*, with two degrees as *bivariant*, with three as *tervariant*, with four as *tetravariant*, and so on. The main interest in these to the student of phase diagrams is to know that on the diagrams the loss of a dimension means the loss of a degree of freedom. Dimensions may be lost by regular progression from a space to a plane or a surface, thence to a line or curve, and finally to a point. This will be understood better as the actual examples are studied.

To avoid confusion it should be noted that the above terms invariant, univariant, etc., may be used with certain restrictions which give different meanings to them. Thus, as already stated, pressure has been excluded from discussions in this book. This restriction is indicated by the term "condensed" and therefore an invariant condensed system would be univariant if pressure were included. Similarly, if temperature is fixed the degree of freedom may be qualified by the term "isothermal." In this sense an invariant isothermal condensed system would be univariant condensed. This will also be understood better when the examples are studied. It will then be seen that an isothermal invariant point on an isothermal diagram is different from the system invariant point of a polythermal diagram. The former would be univariant on the polythermal diagram.

The following is an attempt to express in a few words the principles of phase diagrams and their application. The phase isotherm shows the boundaries of fields of different phases and gives exact information about any possible mixture of the components at the specified temperature. The whole diagram is a system; but a point representing a particular mixture under consideration is also a system. This system (complex) can be moved about within the whole system by such methods as adding or removing one of the components, say water, or by removing one of the phases, e.g. by filtration or settling. Changing the temperature, that is considering another isotherm, does not move the point representing the system being studied, but it moves the boundaries of the fields and so the point has been altered relative to the phase boundaries. The following chapters set out to amplify this statement, commencing with the binary system of one salt and water and leading up to the quinary beyond which the student should be able to make his own way by a process of "extrapolation."

For the student who wishes to check his phase reactions by the phase rule we suggest he use the modified form for condensed systems, as explained in Chapter XIII,

$$F = C - P + 1$$

## CHAPTER II

### TWO-COMPONENT DIAGRAMS

As this book sets out only to deal with equilibrium in aqueous solutions, the two-component system to be considered is that of water and a chemical substance, usually a salt. The phase diagram in this case is the familiar solubility curve of elementary textbooks, but it is much more than just the curve, and every point on the diagram has a quantitative meaning. For this reason and because it is the foundation for more complicated diagrams, the graphical representation of the two-component system will be described in detail and from first principles.

A solubility curve is plotted within a rectangular figure the top of which is usually left open. Temperature is measured from the base upwards and the composition of the solution, in terms of per cent. salt and water, is measured between the two vertical sides of the figure.

The distance between the two verticals is considered as being divided into one hundred parts, percentages of the salt being measured from left to right and percentages of water from right to left. The base line is taken to represent any convenient temperature.

A moment's consideration will make clear that this procedure is not quite the same as plotting a curve on graph paper using the more common rectangular co-ordinates of each point. In that case one horizontal axis  $X$  and one vertical axis  $Y$  have an origin marked  $O$  and taken as the zero point for both  $X$  and  $Y$ . With a diagram such as Fig. 1 there are two verticals, one representing 100% water and the other 100% of the salt, and these two verticals are definite boundaries of the system.

Squared paper is convenient for this type of diagram, and the paper divided into centimetre squares subdivided into millimetres is useful. The two verticals are drawn so that the distance between them is ten squares or a multiple of ten squares and any convenient scale may be chosen for the temperature. Squared paper is not essential and very good diagrams can be made on the drawing board, the points being plotted with T-square and set-square or in the absence of these with a pair of compasses or a parallel rule.

For convenience the percentages of the salt are marked along the base, the left-hand side being the water vertical and the right-hand side the salt vertical. Between these two vertical lines the composition of any mixture of water and the salt may be represented, but the composition is denoted by a *vertical line* and not by a point. Temperature is measured from the base and it is usual to mark the temperature scale along the left-hand vertical, but here again it must be noted that a temperature is a *horizontal line* and not a point. The composition of a solution, or a mixture of water and the salt, at a definite temperature becomes a point.

The solubility curve is plotted from data which should state the percentage composition of saturated solutions at various temperatures. Each point is plotted at the position where the composition vertical is crossed by its corresponding temperature line. When all the points have been marked a curve is drawn evenly through them.

In almost all cases there will be one or more breaks in the curve or, in other words, there will be more than one curve. The solubilities of a very large number of salts have been determined over a range of temperature and published in standard reference books.

# AQUEOUS SOLUTION AND THE PHASE DIAGRAM

In most cases the points at which the curves break are given as a definite temperature and composition. In such cases the drawing of the curve presents no difficulties.

TABLE I  
AMMONIUM SULPHATE AND WATER  
(From Landolt-Börnstein, I, 669)  
Composition of saturated solutions at various temperatures.

Temperature °C.	$(\text{NH}_4)_2\text{SO}_4$ g. per 100 g. Solution.	Solid Phase.
- 5.45 . . . . .	16.7	Ice
- 11 . . . . .	28.6	"
- 18 . . . . .	37.5	"
- 19.05 . . . . .	38.4	Ice + $(\text{NH}_4)_2\text{SO}_4$
0 . . . . .	41.4	$(\text{NH}_4)_2\text{SO}_4$
+ 10 . . . . .	42.2	"
20 . . . . .	43.0	"
30 . . . . .	43.8	"
40 . . . . .	44.8	"
50 . . . . .	45.8	"
60 . . . . .	46.8	"
70 . . . . .	47.9	"
80 . . . . .	48.8	"
90 . . . . .	49.8	"
100 . . . . .	50.8	"
108.9 . . . . .	51.8	" Boiling-point

Table I gives the percentages of ammonium sulphate in saturated solutions at various temperatures. These figures are used to plot points on the diagram, Fig. 1. The two curves are then drawn through the two sets of plotted points.

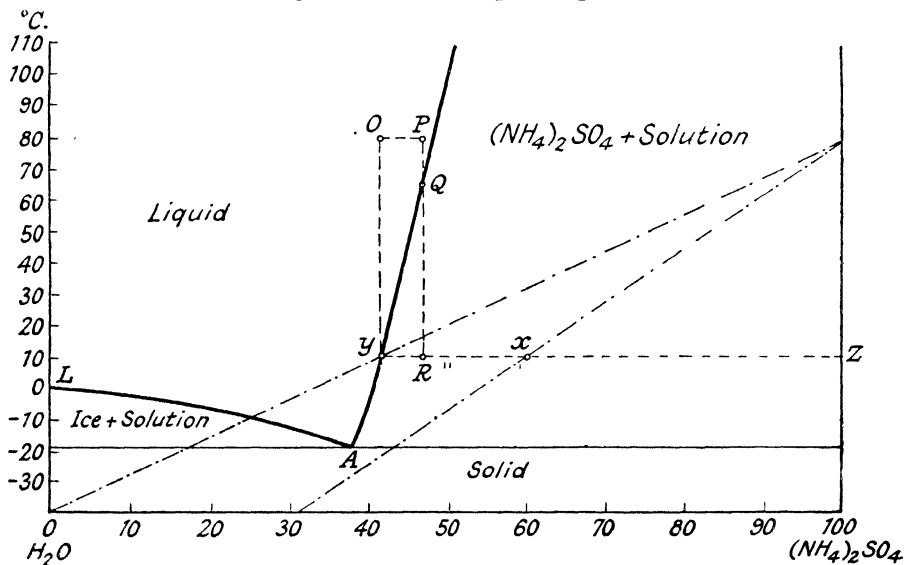


FIG. 1.— $(\text{NH}_4)_2\text{SO}_4$ -water.

Such lines are referred to as *curves* even though in some cases they may appear to be straight lines. This is to avoid any confusion between such curves and actual straight lines which are used on phase diagrams.

Such solubility curves in which the concentration of a saturated solution is plotted against temperature are very familiar but their full use is sometimes overlooked. For instance, too much attention is paid to the curve itself without it being realized that *every point on the diagram has significance*, whether it lies on the curve or not. Thus any proportion of a simple salt to water at any given temperature may be marked on the graph paper by a point. By noting the relation of the point to the curve, one may predict the final condition of such a mixture, that is, what the solution will be, and how much and what solid.

For the sake of regularity it must be repeated that, in addition to temperature and concentration, there is another factor, pressure. Throughout this work pressure is ignored because for this particular aspect of the Phase Rule the effect of pressure is negligible. As a definite example of this the solubility of zinc sulphate at 25° C. and atmospheric pressure is 36.69%, whereas its solubility at 25° C. at 250 atmospheres is 36.66%. The figures for sodium chloride are 26.42% and 26.59% under the same conditions.

On the other hand, the vapour phase is considerably affected by pressure and so, by ignoring pressure, we are assuming a system where there is no vapour phase. Such a system is called a *condensed system*. With water solutions this means that the water can be taken as all condensed, i.e. liquid or solid. Atmospheric pressure is generally taken to fulfil this condition.

**A Simple Case without Hydrates.** Table 1, as already stated, gives the solubility of ammonium sulphate and Fig. 1 is the solubility curve plotted therefrom. Fig. 1 is usually called a solubility curve, but it is just as much a phase diagram as are some of the more complicated diagrams given later in this book. The use of such a diagram is to be able to determine what will happen to any mixture of ammonium sulphate and water at any temperature.

The right-hand curve is the more familiar one as the left-hand one is often ignored. The former curve is the solubility of ammonium sulphate, the latter being the "solubility" of ice in weak ammonium sulphate solutions. The latter curve is also called the freezing-point curve. This means that any solution of ammonium sulphate to the left of point *A*, when cooled, will deposit ice and not ammonium sulphate. To complete the diagram a horizontal straight line is drawn through the point *A* from the vertical line representing 100% water to the vertical line representing 100% ammonium sulphate.

Fig. 1 has been marked in a qualitative fashion to show what is to be expected in the various parts of the diagram. The lines and curves divide it into a number of *fields*. The upper field above the two curves is marked liquid and this means that any solution, which is at such a temperature that it comes within this field, is completely liquid with no solid and is an unsaturated solution.

The lowest field is completely solid and any mixture of ammonium sulphate and water may come within this field, but it will be noticed that such a mixture is only completely solid when it is below the temperature of *A*, i.e. below -19° C. The point *A* is called the eutectic point, the corresponding temperature being the eutectic temperature, and the corresponding mixture of ice and ammonium sulphate the eutectic mixture. It is important to realize that the eutectic mixture is a *mixture* and not a compound. The compounds are at the peaks of curves as will be seen later.

Within the field to the right marked " $(\text{NH}_4)_2\text{SO}_4$  + solution," ammonium sulphate crystals exist in equilibrium with a saturated solution. Within the left-hand field marked "ice + solution" solid ice exists in equilibrium with a solution of ammonium sulphate. The latter solution is saturated with respect to ice but not saturated with respect to ammonium sulphate. These two fields are the only ones where it is necessary to determine the relation of solid to liquid: we propose to take an example from the right-hand one.

Suppose the mixture to be:

60 g. ammonium sulphate
40 g. water
—
100 g.
—
at $10^\circ \text{C}$ .

This is plotted as point  $x$  on the diagram. At this point there will exist solid ammonium sulphate and saturated solution at  $10^\circ \text{C}$ . A line drawn through point  $x$  along the  $10^\circ \text{C}$ . line cuts the curve at  $y$  where the ammonium sulphate content is 42.2%. This, then, is the composition of the saturated solution.

The proportion of solid ammonium sulphate to solution may also be determined. Produce the  $10^\circ \text{C}$ . line to meet the 100% ammonium sulphate vertical at  $z$  and measure  $xy$  and  $xz$ . Then the proportion of solid to liquid will be in the proportion of  $xy$  to  $xz$ . In the case taken

$xy$ measures 18 (units of the abscissa scale)
$xz$ measures 40
—
58
—

so that there will be

18 parts of solid ammonium sulphate
to 40 parts of solution containing 42.2% ammonium sulphate
in 58 parts of mixture.

The above figures are converted into percentages by simple proportion as follows:

58 parts mixture contain 18 parts solid and 40 parts solution
100    "        "        " $\frac{18 \cdot 100}{58}$ "        "        " $\frac{40 \cdot 100}{58}$ "        "
i.e. 31 parts solid and 69 parts solution.

The percentages of solid ammonium sulphate and solution may also be read from the diagram, thus avoiding the above calculation. A simple way of doing this is to draw a straight line from the point representing 0% ammonium sulphate on the base line, through  $y$  to cut the vertical line representing 100% ammonium sulphate at a point which we call the projection point. From this projection point draw a straight line through  $x$  to cut the base line. The point on the base line, so obtained, will be, in this example, 31% and we interpret this as 31% ammonium sulphate solid and 69% solution of composition  $y$ .

The above remarks apply to the field bounded by the right-hand curve of the diagram. The field associated with the left-hand curve may be treated in a similar manner. Take a point in the "ice + solution" field to represent a mixture at a specified temperature. Through this point draw a horizontal line from the water vertical (the left-hand vertical) to the curve. The point where this line meets the curve gives the composition of the

solution, that is, the liquid phase. The proportions of ice and solution are found by measuring the distance from the curve to the original point (towards ice) for the proportion of ice and from the water vertical to the point (towards solution, i.e. the curve) for the proportion of solution.

So far we have only indicated how points on the diagram are read. The practical use of two-component diagrams is considered in Chapter III, but it may not be out of place to give one example at this stage.

A solution or mixture which is heated or cooled still maintains the same composition even though the proportions of solid and liquid may vary. Therefore change of temperature can only take place along vertical lines, these being lines of constant composition.

As an example, if a hot solution of ammonium sulphate is cooled, cooling can only take place along a vertical line from the point representing the composition of the solution. Take a point *P* at 80° C. within the liquid field. The solution is not saturated but as the solution cools it will follow the vertical line and so approach the saturation curve, meeting the curve at *Q* which happens to be at 65° C. At this point the solution is saturated, and on further cooling ammonium sulphate will crystallize. If cooling is discontinued at 10° C., the mixture will be represented by the point *R*, which still has the same composition as *P*. The mother liquor will have composition *y* and the proportions of solid ammonium sulphate and mother liquor will be given by the distances *yR* and *zR*, as already studied in the earlier example.

It may be noted here that when a solution, such as that represented by the point *P*, is allowed to cool, there is a change in the rate of cooling when the temperature reaches that represented by the point *Q*. A further change in rate of cooling would occur at the eutectic temperature — 19° C. This is illustrated in Fig. 1*a*, which is further explained in the section on thermal analysis, p. 69 *et seq.*

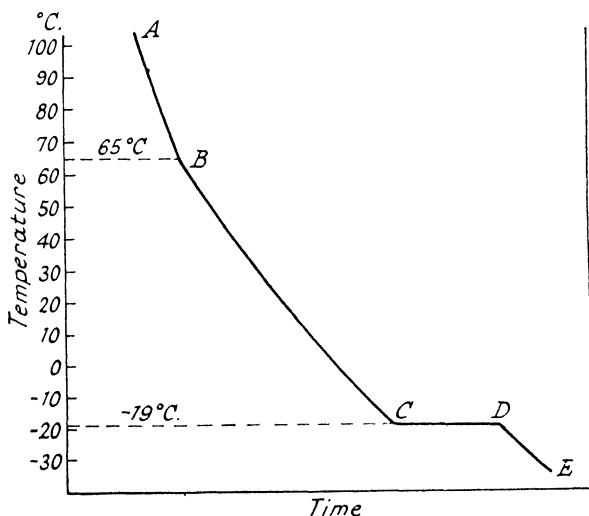


Fig 1*a*.—Cooling curve for solution of 47.3%  $(\text{NH}_4)_2\text{SO}_4$ .

**With Hydrate Formation.** Table 2 gives the solubility of manganese nitrate and Fig. 2 is the diagram plotted therefrom. This example differs from the previous one in

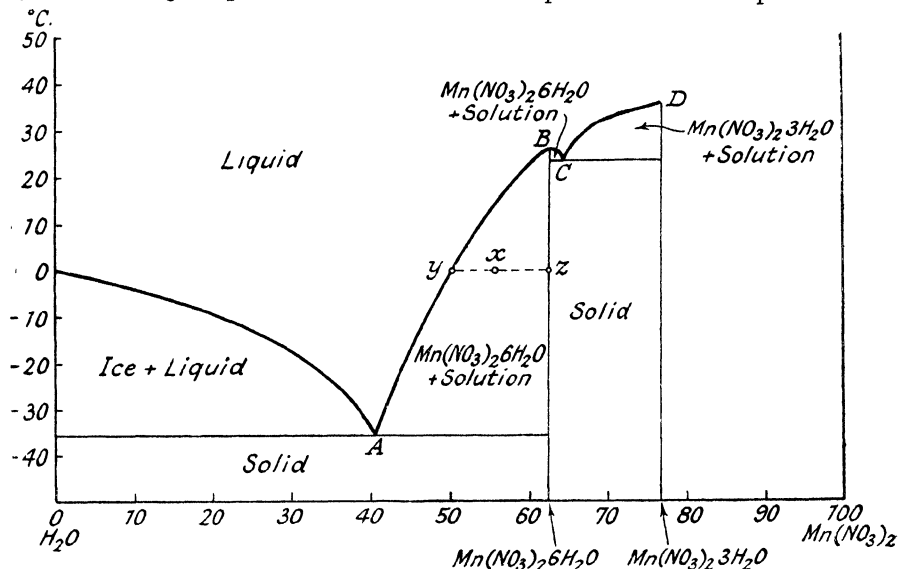


FIG. 2.— $\text{Mn}(\text{NO}_3)_2$ -water.

that hydrates are formed and the manganese nitrate curve is therefore not a single curve but comprises two curves, one for the tri-hydrate  $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and one for the hexahydrate  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The diagram has not been taken beyond the trihydrate as the figures are not available for this.

TABLE 2  
MANGANESE NITRATE AND WATER  
(From Landolt-Bornstein, I, 667)

Composition of saturated solutions at various temperatures

Temperature °C.	$\text{Mn}(\text{NO}_3)_2$ g. per 100 g. Solution	Solid Phase.
-10 . . . . .	21.3	Ice
-20 . . . . .	33.0	"
-36 . . . . .	40.5	Ice + $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
-29 . . . . .	42.3	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
-16 . . . . .	45.5	"
0 . . . . .	50.5	"
+11 . . . . .	54.6	"
25.8 . . . . .	62.4	"
23.5 . . . . .	64.6	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
27 . . . . .	65.6	$\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
30 . . . . .	67.4	"
35.5 . . . . .	76.8	"

Hexahydrate ( $6\text{H}_2\text{O}$ ) = 62.3%  $\text{Mn}(\text{NO}_3)_2$ .  
Trihydrate ( $3\text{H}_2\text{O}$ ) = 76.8%  $\text{Mn}(\text{NO}_3)_2$ .



Having drawn the curves from the figures in the table it is then necessary to mark the positions for the two hydrates on the base and to draw two vertical lines to represent them. The hexahydrate,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , contains 62.3% manganese nitrate and 37.7% water. The trihydrate,  $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , contains 76.8% manganese nitrate and 23.2% water. These values are marked on the base line. Vertical lines are drawn from these points to meet the curves and it will be noticed that the hexahydrate vertical meets its curve at the peak. The trihydrate vertical also meets its curve at the peak, although this is not so obvious as the curve is not drawn beyond this point.

The diagram is completed by drawing two horizontal lines, one through the eutectic point *A* from the water vertical to the hexahydrate vertical and the other through the eutectic point *C* between the verticals of the two hydrates.

The lines and curves divide the diagram into a number of fields. For simplicity the whole diagram may be regarded as composed of two simple diagrams like Fig. 1. Thus one such is between the water vertical and the hexahydrate vertical showing the equilibrium between water and the hexahydrate. Another diagram lies between the hexahydrate vertical and the trihydrate vertical showing the equilibrium between the two hydrates. By this simplification of the diagram any point on Fig. 2 may be examined by the methods already described for Fig. 1.

The various fields have been named on the diagram, but there are two features which require explanation. These are the two hydrate verticals which are marked  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . These lines represent pure solid hydrates and may be regarded as fields having length but no breadth.

The melting-point of the hexahydrate is  $25.8^\circ\text{C}$ . which is marked as point *B*. Above this temperature the compound is all liquid, whereas below it the compound is wholly solid, the melting-point being sharply defined. Thus the hexahydrate vertical represents the solid hexahydrate right up to the temperature of *B*. This feature is especially emphasized because there are two fields marked " $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{solution}$ ," and the infinitely narrow field of the solid hexahydrate separates these two fields.

To carry the above argument a stage further, if there is a trace of the trihydrate with the hexahydrate then the mixture will not be *wholly solid* until it is cooled to the eutectic temperature of  $23.5^\circ\text{C}$ ., there being a mixture of solid hexahydrate and solution between  $25.8^\circ\text{C}$ . and  $23.5^\circ\text{C}$ . On the other hand, if a small amount of water is added to the hexahydrate the mixture will not be wholly solid until it is cooled to the other eutectic temperature of  $-36^\circ\text{C}$ ., there being a mixture of solid hexahydrate and solution between  $25.8^\circ\text{C}$ . and  $-36^\circ\text{C}$ .

Similarly, the trihydrate vertical below *D* represents the solid trihydrate, the melting-point of the compound being  $35.5^\circ\text{C}$ .

In Fig. 2 there are two eutectics, one at *A*, the other at *C*. This, therefore, is the "ideal" phase diagram for two components where hydrates are formed and it is a comparatively rare example. More usually the curves are discontinued before reaching the compound peak. If the curve passes the peak there must be a eutectic.

Before leaving Fig. 2 one quantitative example might be taken. Let the point *x* represent a mixture of manganese nitrate and water at  $0^\circ\text{C}$ . The horizontal line *yz* is drawn through *x*, the point *y* thus representing the composition of the solution. The distance *zx* represents the proportion of solution *y* and the distance *yz* represents the proportion of solid which, in this case, is the hexahydrate.

$$zx = 7.5 \text{ units (of the abscissa scale)}$$

$$yz = 5.0 \text{ units}$$

Therefore there are 7.5 parts of solution of composition  $y$  and 5.0 parts of solid hexahydrate.

**With Hydrates but without Eutectics (Incongruent Melting-points).** In the last example a eutectic mixture was formed between the hydrates. More commonly no such eutectic mixtures occur, the only eutectic point being that between water and the first hydrate. The system of sodium iodide and water may be taken as typical of this class.

Table 3 gives the solubility of sodium iodide and Fig. 3 is the phase diagram. Here, again, there are two hydrates, a pentahydrate,  $\text{NaI} \cdot 5\text{H}_2\text{O}$ , and a dihydrate,  $\text{NaI} \cdot 2\text{H}_2\text{O}$ , and these have to be marked on the base and vertical lines drawn therefrom.

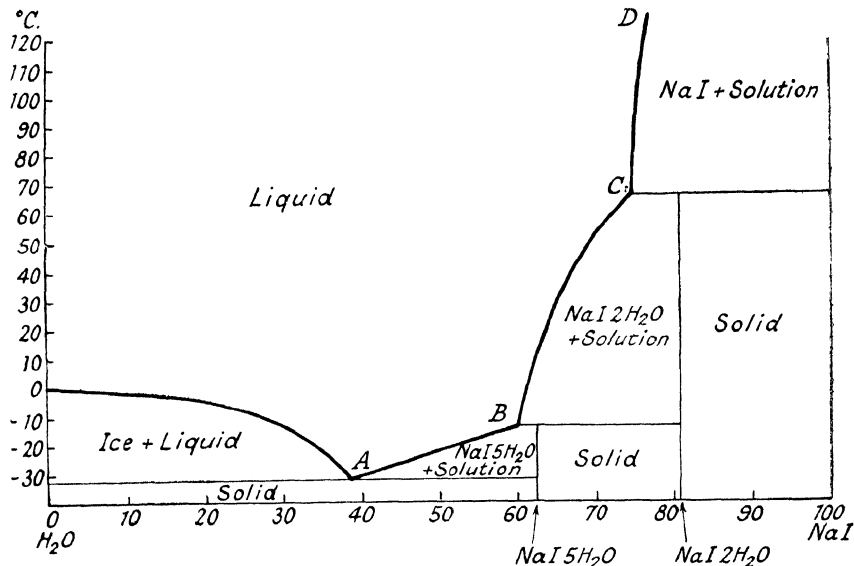


FIG. 3.—NaI water.

The pentahydrate vertical does not meet its own curve  $AB$ , nor does the dihydrate vertical meet its own curve  $BC$ . The former vertical is therefore not taken beyond the temperature of point  $B$ , while the latter is not taken beyond the temperature of point  $C$ . This is because the pentahydrate cannot exist above the temperature of  $B$ , nor the dihydrate above the temperature of  $C$ .

To complete the diagram the pentahydrate vertical, as mentioned above, is not drawn beyond the temperature line passing through the transition point  $B$ . From  $B$  a horizontal line is drawn, meeting the pentahydrate vertical and produced to meet the vertical representing the next compound, in this case the dihydrate vertical.

In the same way the dihydrate vertical is not taken beyond the temperature line passing through  $C$  and from  $C$  a horizontal line is drawn to meet the vertical representing the next compound, in this case the anhydrous salt.

Finally, a horizontal line is drawn through the point  $A$ , the eutectic between water and the first hydrate, and the line produced to meet the water vertical on the left and the pentahydrate vertical on the right.

TABLE 3

SODIUM IODIDE AND WATER  
(From Landolt Börnstein, I, 673)

Composition of saturated solutions at various temperatures.

Temperature ° C.	NaI g. per 100 g. Solution.	Solid Phase.
— 4.25 . . . . .	14.6	Ice
— 9.75 . . . . .	26.5	"
— 31.5 . . . . .	39	Ice + NaI.5H <sub>2</sub> O
— 15.2 . . . . .	57.2	NaI.5H <sub>2</sub> O
— 13.5 . . . . .	60.2	NaI.5H <sub>2</sub> O + NaI.2H <sub>2</sub> O
0 . . . . .	61.3	NaI.2H <sub>2</sub> O
0 . . . . .	61.4	"
+ 10 . . . . .	62.8	"
20 . . . . .	64.2	"
30 . . . . .	65.5	"
40 . . . . .	67.2	"
50 . . . . .	69.5	"
60 . . . . .	72.0	"
60 . . . . .	72.0	"
65 . . . . .	74.4	NaI.2H <sub>2</sub> O + NaI
80 . . . . .	74.7	NaI
100 . . . . .	75.1	"
100 . . . . .	75.4	"
120 . . . . .	76.3	"
140 . . . . .	77.2	"
140 . . . . .	76.9	"
141 . . . . .	—	" Boiling-point

NaI.5H<sub>2</sub>O = 62.5% NaI.

NaI.2H<sub>2</sub>O = 80.6% NaI.

TABLE 4

COPPER NITRATE AND WATER  
(From Landolt-Börnstein, I, 651)

Composition of saturated solutions at various temperatures.

Temperature ° C.	Cu(NO <sub>3</sub> ) <sub>2</sub> g. per 100 g. Solution.	Solid Phase.
— 2.35 . . . . .	8.0	Ice
— 9.3 . . . . .	21.3	"
— 20.0 . . . . .	34.3	"
— 24.0 . . . . .	35.9	Ice + Cu(NO <sub>3</sub> ) <sub>2</sub> .9H <sub>2</sub> O
— 21.0 . . . . .	37.4	Cu(NO <sub>3</sub> ) <sub>2</sub> .9H <sub>2</sub> O
— 20.0 . . . . .	39.8	Cu(NO <sub>3</sub> ) <sub>2</sub> .9H <sub>2</sub> O + Cu(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O
0 . . . . .	45.0	Cu(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O
+ 20.0 . . . . .	55.6	"
24.5 . . . . .	61.4	Cu(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O + Cu(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O
40.0 . . . . .	61.5	Cu(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O
60.0 . . . . .	64.2	"
80.0 . . . . .	67.5	"
114.5 . . . . .	77.6	"

Cu(NO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O = 53.7% Cu(NO<sub>3</sub>)<sub>2</sub>.

Cu(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O = 63.5% Cu(NO<sub>3</sub>)<sub>2</sub>.

Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O = 77.7% Cu(NO<sub>3</sub>)<sub>2</sub>.

Any mixture coming within the field marked " $\text{NaI} \cdot 5\text{H}_2\text{O} + \text{solution}$ " is examined by taking its relation to the curve  $AB$  and the pentahydrate vertical by the usual method of drawing a horizontal line through the point under consideration, as described for Figs. 1 and 2. The field marked " $\text{NaI} \cdot 2\text{H}_2\text{O} + \text{solution}$ " is treated in a similar manner.

Finally, any mixture coming within the field marked " $\text{NaI} + \text{solution}$ " is examined in its relation to the curve  $CD$  and the 100% sodium iodide vertical.

The temperatures at  $B$  and  $C$  are called *incongruent melting-points*. This means that the solids,  $\text{NaI} \cdot 5\text{H}_2\text{O}$  and  $\text{NaI} \cdot 2\text{H}_2\text{O}$ , cannot exist in equilibrium with solutions of the same composition. Thus if the solid  $\text{NaI} \cdot 5\text{H}_2\text{O}$  is heated it will decompose into  $\text{NaI} \cdot 2\text{H}_2\text{O}$  and a solution of lower  $\text{NaI}$  content at a temperature ( $B$ ) below its melting-point on the curve  $BC$ . By the time the temperature has reached a point to give  $\text{NaI} \cdot 5\text{H}_2\text{O}$  as solution, then all the solid phase will have disappeared. An incongruent melting-point may be defined as the temperature at which a compound decomposes. Further examples of incongruency will be seen later in the ternary system. (See incongruently saturated solution, p. 39.)

Conversely, a compound is said to have a *congruent melting-point* if the solid and liquid of the same composition can exist together in a state of equilibrium. The point  $B$  on Fig. 2 was a congruent melting-point. In this case the melting-point is sharply defined and distinct.

Another example of the incongruent type of diagram is given in Table 4 and Fig. 4—copper nitrate.

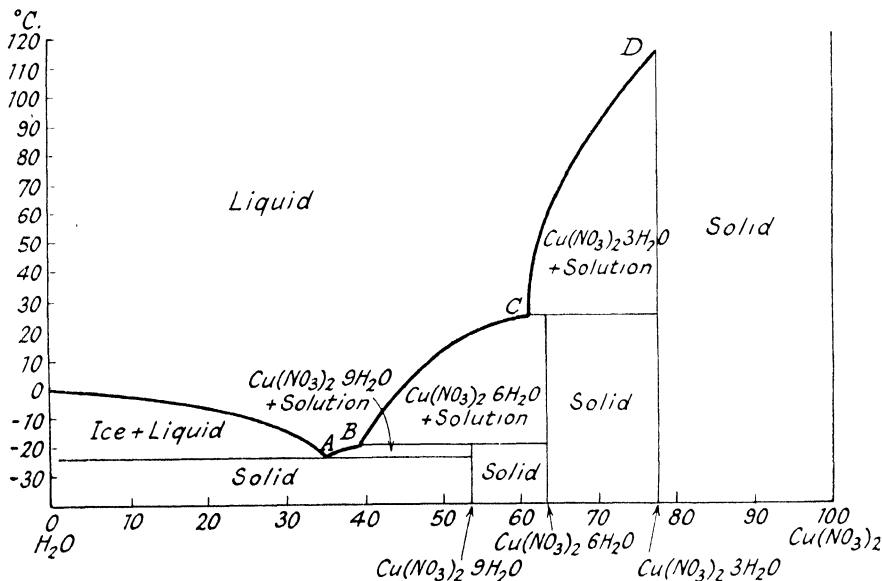


FIG. 4.— $\text{Cu}(\text{NO}_3)_2$ -water.

**Retrograde Solubility.** So far in all the examples given there has been an increase in solubility with rise in temperature. This is the generally expected case, but some salts,

such as sodium sulphate and ferrous sulphate, behave in the opposite way between certain temperatures.

Table 5 gives the solubility of ferrous sulphate and Fig. 5 is the diagram plotted from

TABLE 5  
FERROUS SULPHATE AND WATER  
(From Landolt-Bornstein, I, 652)  
Composition of saturated solutions at various temperatures.

Temperature ° C.	FeSO <sub>4</sub> g. per 100 g. Solution.	Solid Phase.
- 0.7 . . . . .	5.18	Ice
- 1.3 . . . . .	9.47	"
- 1.8 . . . . .	12.99	Ice + FeSO <sub>4</sub> .7H <sub>2</sub> O
0 . . . . .	13.53	FeSO <sub>4</sub> .7H <sub>2</sub> O
+ 10 . . . . .	17.02	"
20 . . . . .	21.0	"
30 . . . . .	24.78	"
40 . . . . .	28.67	"
50 . . . . .	32.7	"
52 . . . . .	33.42	"
54 . . . . .	34.25	"
56.17 . . . . .	35.32	FeSO <sub>4</sub> .7H <sub>2</sub> O + FeSO <sub>4</sub> .4H <sub>2</sub> O
60 . . . . .	35.46	FeSO <sub>4</sub> .4H <sub>2</sub> O
64 . . . . .	35.65	FeSO <sub>4</sub> .4H <sub>2</sub> O + FeSO <sub>4</sub> .H <sub>2</sub> O
68 . . . . .	34.35	FeSO <sub>4</sub> .H <sub>2</sub> O
77 . . . . .	31.46	"
80.4 . . . . .	30.35	"
85 . . . . .	28.8	"
90 . . . . .	27.15	"

FeSO<sub>4</sub>.7H<sub>2</sub>O = 54.6% FeSO<sub>4</sub>.

FeSO<sub>4</sub>.4H<sub>2</sub>O = 67.8% FeSO<sub>4</sub>.

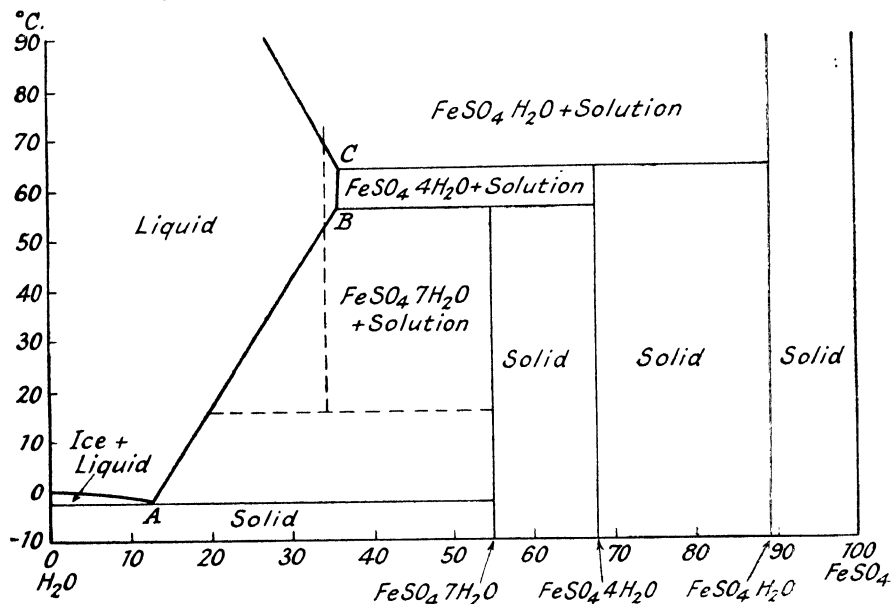
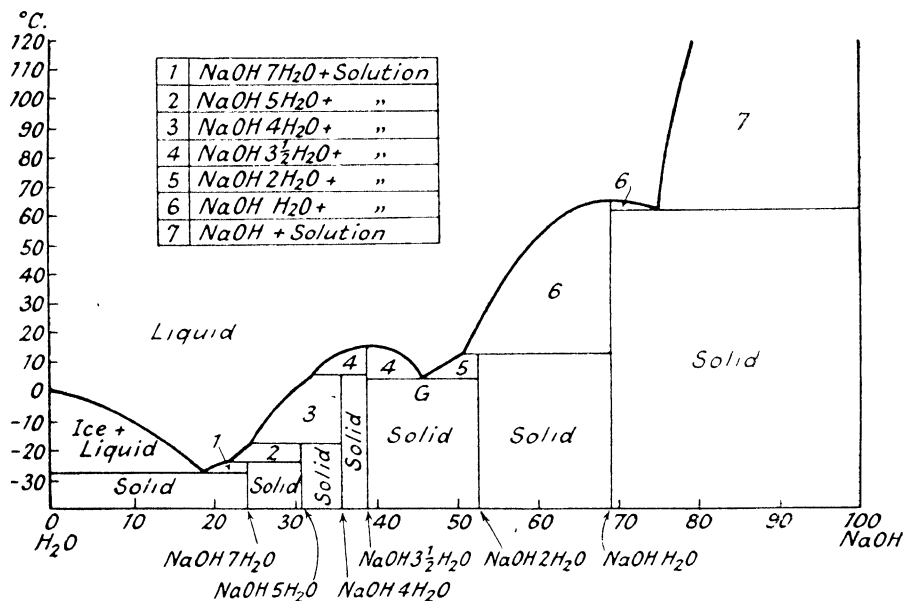
FeSO<sub>4</sub>.H<sub>2</sub>O = 89.4% FeSO<sub>4</sub>.

the data. In this case it is the monohydrate, FeSO<sub>4</sub>.H<sub>2</sub>O, which has the retrograde solubility.

The curve is divided into three parts: the FeSO<sub>4</sub>.7H<sub>2</sub>O curve is below 56° C., the FeSO<sub>4</sub>.4H<sub>2</sub>O curve is between 56° C. and 64° C., and the FeSO<sub>4</sub>.H<sub>2</sub>O curve is above 64° C. The two lower curves are of the type already studied in that any solution, on either of these curves, when cooled, deposits crystals at once. The uppermost curve is the one showing retrograde solubility. A solution on this curve does not immediately deposit crystals when cooled, but is, in fact, capable of dissolving more ferrous sulphate. In order to obtain crystals of the monohydrate, the solution has to be heated.

Having plotted the curves the diagram is completed as follows. The compositions of the three hydrates are marked on the base and the verticals drawn to represent them. The FeSO<sub>4</sub>.7H<sub>2</sub>O vertical is not drawn beyond the temperature line passing through *B*, and from *B* a horizontal line is drawn meeting the FeSO<sub>4</sub>.7H<sub>2</sub>O vertical and produced to meet the vertical of the next hydrate, FeSO<sub>4</sub>.4H<sub>2</sub>O. The horizontal line from *C* in the same way meets the FeSO<sub>4</sub>.4H<sub>2</sub>O vertical and is produced to meet the vertical for the next hydrate, FeSO<sub>4</sub>.H<sub>2</sub>O.

The dotted line indicates the behaviour of a saturated solution on the FeSO<sub>4</sub>.H<sub>2</sub>O curve on being cooled.

FIG. 5.— $\text{FeSO}_4$ -water.FIG. 6.— $\text{NaOH}$ -water.

**A more Complicated Case.** Sodium hydroxide and water give an example where hydrates are formed, some of which give eutectics while others merely show a break in the curve. Table 6 gives the figures and Fig. 6 is the diagram.

Although this diagram looks and is fairly complicated, by taking the fields *one at a time* it should be obvious that there is nothing in the diagram that the reader does not already understand.

TABLE 6  
SODIUM HYDROXIDE AND WATER  
(From Pickering, *J. Chem. Soc.*, 1893, 63, 890)  
Composition of saturated solutions at various temperatures.

Temperature ° C.	NaOH g. per 100 g. Solution	Solid Phase.
— 5.27 . . . . .	5.78	Ice
— 10.29 . . . . .	10.03	"
— 17.20 . . . . .	14.11	"
— 25.2 . . . . .	18.17	"
— 28.0 . . . . .	19.0	Ice + NaOH. 7H <sub>2</sub> O
— 26.0 . . . . .	19.98	NaOH. 7H <sub>2</sub> O
— 25.2 . . . . .	21.1	"
— 24.0 . . . . .	22.1	NaOH. 7H <sub>2</sub> O + NaOH. 5H <sub>2</sub> O
— 21.7 . . . . .	23.31	NaOH. 7H <sub>2</sub> O
— 19.55 . . . . .	23.97	"
— 18.0 . . . . .	24.7	NaOH. 5H <sub>2</sub> O + NaOH. 4H <sub>2</sub> O
— 12.60 . . . . .	25.47	NaOH. 4H <sub>2</sub> O
— 8.45 . . . . .	26.91	"
+ 1.62 . . . . .	30.38	"
5.40 . . . . .	32.3	NaOH. 4H <sub>2</sub> O + NaOH. 3.5H <sub>2</sub> O
7.00 . . . . .	32.97	NaOH. 3.5H <sub>2</sub> O
13.2 . . . . .	35.51	"
15.55 . . . . .	38.83	"
13.95 . . . . .	42.28	"
10.75 . . . . .	44.22	"
5.00 . . . . .	45.5	NaOH. 3.5H <sub>2</sub> O + NaOH. 2H <sub>2</sub> O
7.80 . . . . .	47.3	NaOH. 2H <sub>2</sub> O
10.30 . . . . .	49.11	"
12.30 . . . . .	50.8	NaOH. 2H <sub>2</sub> O + NaOH. H <sub>2</sub> O
18.00 . . . . .	51.7	NaOH. H <sub>2</sub> O
40.25 . . . . .	56.44	"
57.85 . . . . .	62.85	"
63.23 . . . . .	66.45	"
64.3 . . . . .	68.49	"
63.0 . . . . .	71.17	"
62.0 . . . . .	74.2	NaOH. H <sub>2</sub> O + NaOH
80.0 . . . . .	75.83	NaOH
110.0 . . . . .	78.15	"
159.0 . . . . .	81.09	"
192.0 . . . . .	83.87	"

NaOH. 7H<sub>2</sub>O = 24.1% NaOH.  
 NaOH. 5H<sub>2</sub>O = 30.7% NaOH.  
 NaOH. 4H<sub>2</sub>O = 35.7% NaOH.  
 NaOH. 3.5H<sub>2</sub>O = 38.9% NaOH.  
 NaOH. 2H<sub>2</sub>O = 52.7% NaOH.  
 NaOH. H<sub>2</sub>O = 69.0% NaOH.

## CHAPTER III

### SOME PRACTICAL APPLICATIONS

Before going into detail in the use of two-component diagrams it may be well to ask the question—what is generally required to be done with a solution or mixture of one salt and water? Among the more common requirements are the preparation or purification of the salt or one of its hydrates, the maintenance of a system as liquid or as a solid and the concentration of a solution by the removal of water as ice. In order to attain any of these or other results the number of operations that can be used is strictly limited. These are:

Change of temperature.

Addition of water.

Removal of water (or addition of salt).

Change of pressure is not included, as all systems under consideration in this work are assumed to be at constant pressure (see note on condensed systems, p. 9).

In applying the above operations to a phase diagram there are two important rules:

Rule (1). Change of temperature moves the point under consideration along a vertical line, the composition remaining unchanged. Thus raising the temperature moves the point vertically upwards and lowering the temperature moves the point vertically downwards.

Rule (2). Change of water content moves the point under consideration along a horizontal line, the temperature remaining unchanged. Addition of water moves the point horizontally towards the water vertical. Removal of water or addition of the salt moves the point horizontally towards the 100% salt vertical.

An example of rule (1) may be found on p. 11 with reference to Fig. 1. There the temperature was changed from 80° C. to 10° C., the point moving vertically downwards from point *P* to *R*. At *R* the point represented a mixture of solid and liquid. The composition of the combined solid and liquid at *R* was the same as at *P*. The new liquid, of course, had a different composition which was determined by the principles explained in Chapter II.

In order to make rule (2) perfectly clear take the point *x* on Fig. 1. This represents 60% ammonium sulphate and 40% water at 10° C. If water is added to this mixture keeping the temperature at 10° C., the point will move along the 10° C. line, in the direction of *y*. The distance it moves depends upon the amount of water added. If sufficient water is added the point will move beyond *y* and approach the water vertical along *xy* produced.

Conversely, if water is removed, e.g. by exposing the 60% ammonium sulphate solution to a current of dry air, the temperature still being maintained at 10° C., the point will move along the 10° C. line in the direction of *z* and could eventually reach the ammonium sulphate vertical at *z*.

**Crystallization.** In the preparation of a salt by crystallization both rules will be applied. An example will now be taken where it is required to obtain ammonium sulphate crystals from a given weak solution, say 30% ammonium sulphate.

If this solution could be conveniently concentrated in the cold, say at 20° C., it could only be taken as liquid to 43% ammonium sulphate as can be seen on Fig. 1, because the 20° C. line cuts the curve at 43%. By raising the temperature to 100° C. the solution may



be concentrated to 50.8% ammonium sulphate, that being the composition where the 100°C. line cuts the curve.

The procedure, therefore, is to concentrate at a high temperature, say 100°C. or higher, and then to cool the concentrate. This procedure may be outlined on the diagram as follows.

The original solution containing 30% ammonium sulphate lies on the 30% vertical. One would assume that such a solution would be cold when received so that on heating the first movement on the diagram is up the 30% vertical, eventually reaching, say, the 100°C. point. The solution is then concentrated at its boiling-point—this would be just above 100°C., but we will assume it to be 100°C. for the purpose of the diagram. As the solution is concentrated the point on the diagram will move along the 100°C. line towards the ammonium sulphate vertical. (Removal of water—rule 2.) If concentration is to be stopped while the solution still remains liquid then the removal of water must be discontinued when the point moving along the 100°C. line reaches the curve. This is at 50.8%. Actually the concentration would be stopped at about 50% and we will assume that this is so.

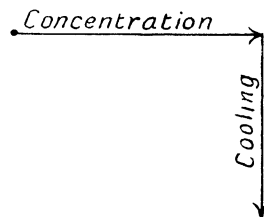
The hot concentrated solution will then be cooled in order to crystallize out the ammonium sulphate. Suppose it is possible to cool to 10°C., then the point on the diagram will move down the 50% vertical from the 100°C. level to 10°C. (Change of temperature—rule 1.) The yield of crystals obtained at 10°C. may be determined by the method described on p. 10.

To summarize : the crystallization of ammonium sulphate by concentration at 100°C. and subsequent cooling of the concentrated solution may be considered on the diagram as the movement of a point along the 100°C. horizontal from 30% to 50% ammonium sulphate, followed by movement of the point down the 50% vertical to the 10°C. position. The following diagram makes this clear :

The above example of concentration and cooling is a very simple case and hardly needed investigation on a phase diagram. It is, however, necessary to understand such a case in order to be able to apply the same principles to a less simple example, as when there are hydrates and it is desired to produce one specific hydrate.

Take Fig. 2, for example. The important feature about this diagram is that it tells one that, if the hexahydrate of manganese nitrate is required, the solution must be concentrated to between *A* and *C*, i.e. between the two verticals representing 40.5% and 64.6% manganese nitrate. If, on the other hand, the trihydrate is required, then the solution must be concentrated to a strength beyond *C*, i.e. beyond the 64.6% vertical. In each case the nearer the concentrated solution is taken to *B* and *D* respectively the greater will be the yield of crystals. If the solution is actually on *B* or *D* then the liquid will be the salt dissolved in its own water of crystallization and when cooled it will set solid, the hexahydrate solidifying at 25.8°C. and the trihydrate solidifying at 35.5°C.

The diagram also indicates the limit to which cooling may be taken. For instance, suppose the solution contains 70% manganese nitrate and that the trihydrate is required. Obviously the solution must be cooled below 32°C., this being where the 70% vertical cuts the curve. It must not, however, be cooled below 23.5°C., this being the eutectic temperature, indicated on the diagram by the horizontal line through the eutectic point *C*, because below this temperature the whole mixture will set solid as a mixture of the two hydrates.



In other words, the cooling must be conducted in such a way that the final solution is at a temperature to bring it within the field marked " $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} + \text{solution}$ ."

The above statement is especially important in preparing the hexahydrate. The greatest yield of crystals is obtained by having the solution as near to *B* as possible, but a study of the diagram shows that whereas a point to the left of *B* may be cooled even to  $-36^\circ\text{C}$ ., a point to the right of *B* may only be cooled to  $23.5^\circ\text{C}$ ., so that the yield of crystals from a solution to the left of *B* will be large while the yield from a solution to the right of *B* will be very small. A solution to the right of *B*, if cooled below  $23.5^\circ\text{C}$ ., will give a solid mixture of the two hydrates.

In cases where there are no eutectics a further advantage of the phase diagram arises. Take, for example, sodium iodide, Fig. 3, and suppose it is desired to obtain the pentahydrate. Here is a case where, if the solution is concentrated until its composition corresponds to the pentahydrate,  $\text{NaI} \cdot 5\text{H}_2\text{O}$ , i.e. 62.5% sodium iodide, the solution will not give the pentahydrate on cooling. A consideration of the diagram shows that such a solution will deposit the dihydrate at  $8^\circ\text{C}$ . and will continue to deposit this compound until the temperature has reached  $-13.5^\circ\text{C}$ .

In order to obtain the pentahydrate the solution must not be stronger than 60% sodium iodide, this being the transition point *B* on the diagram.

It must be admitted that a solution stronger than 60% but weaker than 62.5% sodium iodide if cooled below the temperature of *B*, i.e.  $-13.5^\circ\text{C}$ ., will theoretically give the pentahydrate if equilibrium can be attained between the solid and the liquid, because the final point comes within the field " $\text{NaI} \cdot 5\text{H}_2\text{O} + \text{solution}$ ." This is a problem where the history of the case has to be taken into account. While such a solution was being cooled, between the point on the curve and the  $-13.5^\circ\text{C}$ . horizontal the dihydrate was being precipitated. Below  $-13.5^\circ\text{C}$ . the pentahydrate is precipitated and some of the dihydrate previously formed will be converted to the pentahydrate. The reaction between a solid and liquid is often slow, depending upon the size of crystal, and it is therefore very probable that the final crystals will be contaminated with the lower hydrate.

The first suggestion of using a solution not stronger than 60% is therefore the wiser and safer procedure.

Similarly, the dihydrate is obtained by using solutions between 60% and 74% sodium iodide, i.e. between *B* and *C* on the diagram.

**Purification of Crystals.** Thus far it has been assumed that weak liquors were the source of supply from which crystals were to be obtained. It is perhaps more usual to have impure crystals as the raw material, the problem being to purify them. It may be that the raw material is the wrong hydrate or it may be that there are traces of impurity in them which have to be removed. These impurities may be insoluble in water so that a solution is first prepared and the insoluble matter is filtered or settled out. Or the impurities may be soluble but so small in quantity that they remain in the mother liquor and in such small quantities that they do not materially affect the solubility of the main product. In other words, in spite of the soluble impurity the system can still be considered as one salt and water. The following is such an example.

As the procedure is the same in all cases where the solubility of the salt increases with increase of temperature, for convenience, ammonium sulphate and Fig. 1 can be taken as the example. The recrystallization may first be traced out on this diagram and a convenient temperature and concentration chosen for the hot solution and also a suitable final temperature to which the solution may be cooled.

Let the vertical  $PR$  represent the composition of the hot solution and  $80^{\circ}\text{C}$ . the temperature, that is at the point  $P$ . The solution is not saturated but will become saturated when it has cooled to  $65^{\circ}\text{C}$ ., the point  $Q$  on the curve, and before that temperature is reached the hot solution may be clarified by settling or by filtration.

The clear hot solution is then allowed to cool to the desired temperature, say  $10^{\circ}\text{C}$ ., at which stage the crystals are separated from the mother liquor which is then heated and used to dissolve more of the crude salt. The process is a cyclic one, heating from  $y$  to  $O$ , adding ammonium sulphate from  $O$  to  $P$  and cooling from  $P$  to  $R$ .

The diagram can also be used quantitatively. Starting with, say, one hundred parts of mother liquor represented by the vertical  $Oy$ , 42% ammonium sulphate, it is necessary to add solid ammonium sulphate till the composition of the mixture becomes 47.5% represented by the vertical  $PR$ . The distance  $OP = yR$ , therefore, represents the proportion of solid ammonium sulphate to be added and the distance  $Rz$  the proportion of mother liquor. These distances are 5.5 units for  $yR$  and 52.5 units for  $Rz$  (units are in terms of the abscissa scale).

$$\begin{array}{ccccccc} 52.5 \text{ parts of mother liquor require } 5.5 \text{ parts of ammonium sulphate} \\ 100 & \text{,,} & \text{,,} & \text{,,} & \text{,,} & \text{,,} & \frac{5.5 \times 100}{52.5} \text{ parts of ammonium sulphate} \\ & & & & & & = 10.5 \text{ parts of ammonium sulphate.} \end{array}$$

From the proportions obtained by measurement of the lines  $yR$  and  $Rz$  the amount of ammonium sulphate required can be calculated for any given quantity of mother liquor. After the hot solution has cooled to the desired temperature,  $10^{\circ}\text{C}$ . in this case, the amounts of mother liquor and ammonium sulphate crystals are, of course, the same as before, i.e. 100 parts mother liquor and 10.5 parts crystals.

If the impurities are soluble, even though the percentage is very small, they will accumulate in the mother liquor in time and a stage will eventually be reached when the amount can no longer be ignored. The mother liquor must either be rejected or the impurities removed. The latter may be effected either by a straightforward precipitation or by the application of the principles governing the solubility of two salts and water, which is beyond the scope of this section.

**Desiccation of Crystals. (Solid Processes.)** It is sometimes desired to convert hydrates to the anhydrous state without melting the crystals. This is possible providing their vapour pressure is such that they are capable of giving up their water of crystallization at a temperature low enough to be within the field of "all solid." In such a case the water is removed by the application of vacuum or by subjecting the hydrate to a current of air.

Obviously the quickest result will be obtained when the temperature is as high as possible. The phase diagram gives the necessary information regarding the maximum temperature to be allowed which will ensure the hydrate remaining completely solid throughout the operation.

Take copper nitrate, Fig. 4. The hexahydrate,  $\text{Cu}(\text{NO}_3)_6\text{H}_2\text{O}$ , containing 63.5% copper nitrate will begin to melt at  $24.5^{\circ}\text{C}$ . If the water of crystallization is removed by having the crystals under *vacuo* or by passing a current of dry air over them the diagram shows that liquid will be present if the temperature exceeds  $24.5^{\circ}\text{C}$ ., until the composition reaches the trihydrate  $\text{Cu}(\text{NO}_3)_3\text{H}_2\text{O}$ , i.e. 77.7% copper nitrate. The temperature must therefore be kept just below  $24.5^{\circ}\text{C}$ . until 77.7% is reached, after which the temperature may be raised to  $114.5^{\circ}\text{C}$ ., the point  $D$  on the diagram.

Thus to desiccate any crystals the temperature must be controlled so that it follows the top of the fields marked "solid," being increased by a series of distinct jumps.

**Liquid Processes.** Just as in some cases it is desired to avoid the presence of liquid so in others it is essential to avoid the presence of solids. For instance, in the concentration of a liquid in a complicated plant it is important that the liquid shall remain fluid so that it may flow through the plant without danger of a blockage.

In concentration *in vacuo* there is more danger of crystals being deposited because the boiling-point is reduced. A study of the phase diagram of the solution to be concentrated tells one at once what is the minimum temperature to be specified at any given concentration, and with this knowledge the concentration may be conducted under such a vacuum that the temperature is maintained above that specified.

**Concentration by Removal of Ice.** An interesting, but not common, application of the phase diagram is in the concentration of a solution by the removal of water as ice. This is only applicable where the strength of the original liquor is below that of the first eutectic of the diagram; that is, the concentration vertical must be to the left of point *A* of Fig. 1, Fig. 2, or Fig. 3.

Such a solution on cooling will begin to precipitate ice when the temperature reaches the curve. As the temperature is reduced more ice will be deposited and the concentration of the solution will therefore move to the right. This process may be continued until the concentration of the solution has reached the eutectic point at the eutectic temperature. In practice cooling will be discontinued just above the eutectic temperature so that the ice may be removed by settling or filtration.

As a specific example a 10% ammonium sulphate solution could be concentrated to 27.5% by cooling to  $-10^{\circ}\text{C}$ .

**Solid Fields.** On the diagrams the solid fields have been given compositions. For example, in Fig. 6 one field is stated to contain solid dihydrate and solid 3.5 hydrate. For most practical purposes this is correct because, being solid, any "pure" components or any individual crystals of pure compound cannot be separated from the mixture and the analysis of such a mixture will give the results stated.

It is necessary to point out that equilibrium between solid and solid is not readily attained and will often not be attained unless the mixture has been through a liquid stage or through a stage with some liquid present.

For example, if ice is mixed with anhydrous sodium hydroxide and the temperature maintained below  $-30^{\circ}\text{C}$ ., the mixture will remain as ice and anhydrous sodium hydroxide even though the composition comes between the dihydrate and the 3.5 hydrate. If, however, such a mixture is melted and further heated until it is completely liquid, on re-cooling the mixture of solids will be, as stated on the diagram, the  $2\text{H}_2\text{O}$  and 3.5  $\text{H}_2\text{O}$  compounds.

It is interesting to take the last example in detail and see just what does happen on re-cooling.

If the composition of the solution is to the left of the eutectic point *G*, on cooling the 3.5 hydrate will be deposited first while the composition of the solution moves along the curve towards *G*. When the eutectic temperature is reached the solution will be represented by the point *G* and on further cooling the whole will set solid. In this case the solid mixture may be regarded as composed of the 3.5 hydrate which was first deposited and the eutectic of composition *G*.

Thus the field between *d* and *e* and containing solid dihydrate and solid 3.5 hydrate may be regarded as divided into two fields: that to the left of the *G* vertical is solid 3.5

hydrate + solid eutectic mixture, while that to the left of the  $G$  vertical is solid dihydrate + solid eutectic mixture.

This is not a very important point as mixtures of solids are not easily separated by purely mechanical means, but the reader should have a general idea of what does happen in the completely solid fields.

## CHAPTER IV

### HOW TO USE TRIPLE CO-ORDINATES

Two salts and water, making a system of three components, can only be represented on a plane in two dimensions by omitting the temperature axis. The diagram can conveniently take the form of a triangle when each corner of the figure represents one of the components. The triangle can be of any shape, but the right-angled triangle and the equilateral triangle are the types most generally used, and at this stage it is proposed to use only the equilateral triangle. As the temperature scale is omitted the diagram represents the system at a definite temperature and such a figure is called an Isotherm.

**Triple Co-ordinate Lattices.** Each side of the equilateral triangle is considered as being divided into one hundred equal parts, and lines are drawn parallel to each edge thus forming a lattice, which is referred to as a triple co-ordinate lattice. Triple co-ordinate graph paper is illustrated in Fig. 7, and such paper may be obtained ready ruled from

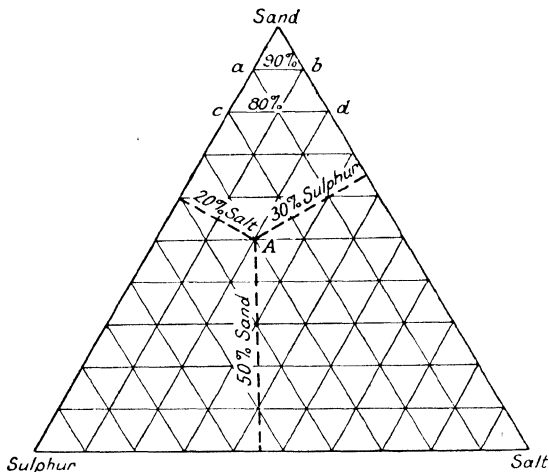


FIG. 7.—Triple Co-ordinate Graph Paper.

scientific booksellers. The peculiar advantage of such an arrangement is that any mixture of three substances can be represented by a point within the triangle. For example, suppose the mixture contain :

30% sulphur  
20% salt  
50% sand

100%

The corners of the triangle will represent pure sulphur, pure salt and pure sand, as

indicated on the diagram. Thus the point at the extreme top of the triangle represents 100% sand ; the other corners represent 100% sulphur and 100% salt respectively. Moving away from the corner marked "sand" the percentage of sand becomes less and less, so that 90% sand is represented on the line *ab* ; 80% sand is on the line *cd* ; and so on, until the bottom line or edge is reached indicating 0% sand.

The percentage contents of sulphur and salt are considered in a similar way, the sulphur figures being read on the lines parallel to the right-hand side of the triangle and the salt figures on the lines parallel to the left-hand side of the triangle. Thus a mixture of the composition given above is represented by the point *A* in Fig. 7. This point is fixed by counting 50 units of the scale *from the base line towards sand* for the sand percentage, 30 units from the right-hand edge *towards sulphur* for the sulphur percentage, and 20 units from the left-hand edge *towards salt* for the salt percentage.

It will be clear from a study of the diagram that the sum of the values for sand, sulphur and salt of *any* point within the triangle must be 100, so that it is possible to place any mixture within the triangle. It is also obvious that any two out of the three percentages are sufficient to fix any particular point. A curve is obtained by plotting a series of points and joining them by a line.

**To Plot a Solubility Curve on Triple Co-ordinates.** A solubility curve on a triple co-ordinate diagram represents the changes in solubility of one salt in water produced by the presence of the other salt and *vice versa*. In Chapters II and III the changes in solubility were caused by changes in temperature and on a two-component diagram at a definite temperature, an isotherm, each curve would have been no more than a point. In a triple co-ordinate diagram a solution saturated with one substance, and with none of the other substance present, is a point, this being on one of the edges of the figure. On adding a second soluble substance some of it will dissolve and the solubility of the original substance will be changed. Therefore the composition of the solution will be represented by a new point, this time within the triangle.

As more and more of the second substance is added a series of new points will be obtained, thus forming a curve. Hence it will be seen that whereas with one salt and water an isotherm is a point, with two salts and water isotherms become curves. These isotherms represent equilibrium between the solid salts and their solutions at one temperature. It may appear at this stage that such diagrams are too restricted to be of much value. This is definitely not so, and in any case methods of including temperature changes will be considered later.

TABLE 7  
SODIUM NITRATE.POTASSIUM NITRATE.WATER  
(From E. Cornec and H. Krombach, *Catuche*, 1928)  
Composition of saturated solutions at 50° C.

Ref. Letter.	NaNO <sub>3</sub> . %	KNO <sub>3</sub> %	Water. %	Solid Phase.
<i>L</i> . . . . .	53.2	0	46.8	NaNO <sub>3</sub>
	47.6	12.3	40.1	"
	43.3	21.6	35.1	"
<i>A</i> . . . . .	39.8	28.9	31.3	NaNO <sub>3</sub> + KNO <sub>3</sub>
	31.7	31.3	37.0	KNO <sub>3</sub>
	19.1	35.9	45.0	"
<i>M</i> . . . . .	0	46.2	53.8	"

Table 7 gives the figures for sodium nitrate and potassium nitrate in water at the temperature of  $50^{\circ}\text{C}$ . From these figures the diagram, Fig. 8, is plotted as follows :

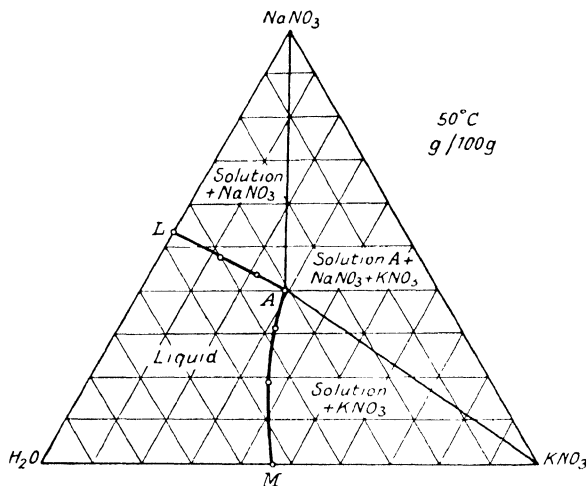


FIG. 8.— $\text{NaNO}_3$ ,  $\text{KNO}_3$ , water.

The point  $L$ , which is marked on both table and diagram, is the straightforward solubility of pure sodium nitrate in water at  $50^{\circ}\text{C}$ . The figures immediately below this give the composition of solutions saturated with sodium nitrate but which contain more and more potassium nitrate. The solutions are not saturated with respect to potassium nitrate. Thus, in this part of the table, the solid phase is given as sodium nitrate, meaning that if any solid sodium nitrate is added it will not dissolve. On the other hand, if a small quantity of potassium nitrate is added it will dissolve. Thus if any solid phase is present in equilibrium with such a solution, that solid must be sodium nitrate.

At the point  $A$  the solution has reached that stage when it is saturated with both sodium and potassium nitrates so that the solid phase is shown as a mixture.

At  $M$  the figure given in the table is the straightforward solubility of potassium nitrate in water at  $50^{\circ}\text{C}$ . The figures immediately above this give the compositions of solutions saturated with potassium nitrate but which contain more and more sodium nitrate. Such solutions are saturated with potassium nitrate but not with sodium nitrate, and the solid phase is therefore marked as potassium nitrate. Finally, the point  $A$  is reached from the other direction.

Each of the points is plotted from the figures in the table and the points joined to form the two curves meeting at  $A$ . To complete the diagram the point  $A$  is joined by a *straight* line to the sodium nitrate corner and by another straight line to the potassium nitrate corner.

The figures in Table 7 are given as percentages by weight. The data is expressed as *composition by weight*, and it is convenient to make the sum of the three components equal to one hundred, but this is not compulsory as it is equally possible to construct the diagram from data in parts per thousand, or in parts of unity, providing each side of the triangle is taken as being equal to one thousand, or to one, as the case may be.



In order to give opportunity for experience in plotting this type of diagram the figures for two more diagrams are given, Table 8 being potassium iodate and potassium iodide,

TABLE 8  
 $\text{KIO}_3, \text{KI}, \text{H}_2\text{O}$  AT  $25^\circ \text{C}$ .  
 (From John E. Ricci, *J.A.C.S.*, 1937, **59**, 867)  
 G. per 100 g. of Solution.

$\text{KIO}_3$ .	KI.	Water.	Solid Phase.
8.45	0	91.55	$\text{KIO}_3$
7.15	2.40	90.45	"
4.33	12.04	83.63	"
3.27	22.38	74.35	"
2.54	41.10	56.36	"
2.35	57.02	40.63	"
2.36	58.51	39.13	$\text{KIO}_3 + \text{KI}$
2.25	58.62	39.13	KI
1.10	59.14	39.76	"
0.0	59.76	40.24	"

TABLE 9  
 $\text{Na}_2\text{CO}_3, \text{K}_2\text{CO}_3, \text{H}_2\text{O}$  AT  $36^\circ \text{C}$ .  
 (From Arthur E. Hill and Frederick W. Miller, *J.A.C.S.*, 1927, **49**, 682)  
 G. per 100 g. of Solution.

$\text{Na}_2\text{CO}_3$ .	$\text{K}_2\text{CO}_3$ .	$\text{H}_2\text{O}$ .	Solid Phase.
0	53.6	46.4	$\text{K}_2\text{CO}_3 \cdot 3/2\text{H}_2\text{O}$
3.5	50.9	45.6	"
4.0	50.4	45.6	$\text{K}_2\text{CO}_3 \cdot 3/2\text{H}_2\text{O} + \text{K}_2\text{CO}_3\text{Na}_2\text{CO}_3$
4.9	48.7	46.4	$\text{K}_2\text{CO}_3\text{Na}_2\text{CO}_3$
5.7	46.5	47.8	"
7.2	45.4	47.4	$\text{K}_2\text{CO}_3\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CO}_3\text{H}_2\text{O}$
9.6	39.5	50.9	$\text{Na}_2\text{CO}_3\text{H}_2\text{O}$
12.9	32.4	54.7	"
18.2	23.4	58.4	"
21.5	17.6	60.9	"
33.2	0	66.8	"

and Table 9 being sodium carbonate and potassium carbonate. Table 9 is a more complicated case and the diagram should not be plotted until after studying Fig. 14.

Numerous other examples can be found in the literature, especially the *Journal of the American Chemical Society* and *Zeitschrift für physikalische Chemie*. Many of the examples given in this book were taken from *Caliche*, a journal published for the Chilean Nitrate Association. A very good book containing the solubility data for systems up to the quaternary is *Solubilities of Inorganic and Metal Organic Compounds*, Vol. 1, by Atherton Seidel, 3rd edition, 1940. Other books giving solubility data are *Dictionary of Chemical Solubilities Inorganic*, 2nd edition, by A. M. Comey and D. A. Hahn, 1921; *Landolt-Börnstein Physikalisch-Chemische Tabellen*, 5th edition, 1923-36; and *International Critical Tables of Numerical Data, Physics, Chemistry and Technology* (McGraw-Hill), 1926-33.

The reader should be warned that sometimes the data are given in ways which may be

wrongly interpreted. For example, if expressed as *molality* it must be remembered that this means gram-mols. per 1,000 grams of solvent and must not be confused with *molarity* which means gram-mols. per litre of solution.

In the examples so far given in each case the two salts have a common ion. They are both salts of the same acid or of the same base. In most cases of three-component systems consisting of two salts and water, the two salts must have a common ion. Such an example as sodium nitrate, potassium chloride, and water is not a case of two salts and water, because by double decomposition both sodium chloride and potassium nitrate can be formed and the system thus becomes one of more than three components. Such systems will be considered in a later chapter.

## CHAPTER V

### HOW TO READ THREE-COMPONENT DIAGRAM

**The Interpretation of a Simple Diagram.** The purpose of this chapter is to show how to read a three-component diagram as a preliminary to its practical application. Any mixture of the two salts and water at a given temperature is represented by a point on the diagram for that particular temperature. The position of this point shows at a glance whether the mixture will be liquid or solid or a mixture of both. In addition, its position indicates the composition of liquid and solid and their proportion.

The mixture of the two salts and water is called a *complex*, and this must be clearly distinguished from the term *solution*. A complex is the complete mixture, whereas the solution is the liquid which that mixture may contain when the mixture has reached equilibrium. In some cases the complex will be all liquid, that is, solution; in others it will be a solution (liquid) and a solid, the solid being either one of the components or a mixture of the two.

The composition of the complex which determines the point must be the percentage composition of the whole mixture. Unless something (water or salt) is *removed* from or *added* to the mixture the composition of the complex cannot alter. The mixture may be heated or cooled, thus altering the proportion of solid to liquid, but the composition of the complex remains fixed, that is, it is represented by a *fixed* point on the diagram.

Proceeding now to an examination of a diagram, Fig. 8 represents a simple type. In examining any complex on the diagram the conclusions arrived at assume that the mixture has been given full opportunity to reach equilibrium between solid and liquid. To effect this the mixture must have been agitated at the specified temperature for a sufficient length of time.

**QUALITATIVE.** The curves and lines divide Fig. 8 into four areas, referred to as fields. A complex situated within the field marked "liquid" is all solution. The three other fields represent mixtures of solids and liquids as follows:

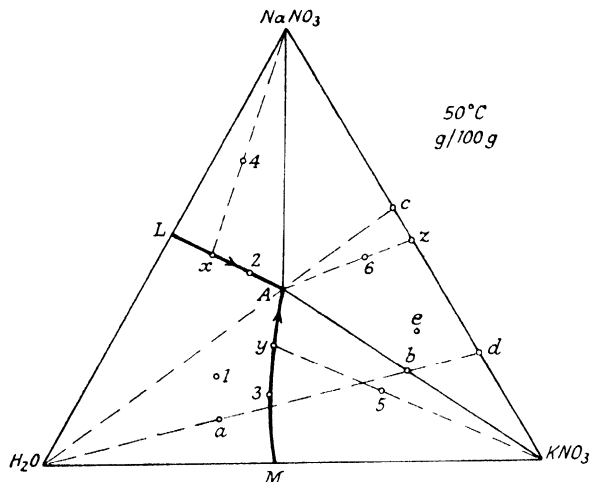
A complex within the triangular field marked "solution +  $\text{NaNO}_3$ " is composed of some solid sodium nitrate and a solution, the solution being somewhere on the curve *LA*.

A complex in the similar, but opposite, field marked "solution +  $\text{KNO}_3$ " is composed of solid potassium nitrate and a solution, the solution in this case being on the curve *MA*.

A complex within the field marked "solution *A* +  $\text{NaNO}_3$  +  $\text{KNO}_3$ " is composed of a mixture of solid sodium nitrate and solid potassium nitrate together with a solution of the composition represented by the point *A*.

In general terms, when the *solid phase is fixed* the *solution is variable* within the limits of the curve bounding the field. Conversely, when the composition of the *solution is fixed* at the invariant point the *solid phase is a mixture* of the two salts. In Fig. 8 the point *A* is the invariant point.

**QUANTITATIVE.** A phase diagram, however, goes further than this and indicates the exact composition of the liquid and solid in any complex. Fig. 8 gives the qualitative description of the various fields; Fig. 9 is the same diagram marked for the quantitative

FIG. 9.— $\text{NaNO}_3$ ,  $\text{KNO}_3$ , water.

examination of points within each of the fields. Point 1 is all liquid and represents an unsaturated solution. In the example given the composition of this solution is :

sodium nitrate . . . . .	20%
potassium nitrate . . . . .	25%
water . . . . .	55%

The point  $L$  is a saturated solution of sodium nitrate with no potassium nitrate, while  $M$  is a saturated solution of potassium nitrate with no sodium nitrate.

Point 2 is a solution similar to  $L$  in that it is saturated with sodium nitrate, but in this case it also contains some potassium nitrate. The composition of this solution is :

sodium nitrate . . . . .	43.7%
potassium nitrate . . . . .	20.0%
water . . . . .	36.3%

Point 3 is saturated with potassium nitrate, but containing some sodium nitrate, the composition being :

sodium nitrate . . . . .	15%
potassium nitrate . . . . .	38%
water . . . . .	47%

The point  $A$  is a special case where the solution is saturated with both sodium nitrate and potassium nitrate. The composition of this solution is given in Table 7.

Any complex on the curves  $LA$  or  $MA$  can be considered as being within the liquid field but, being on the boundary of the field, it is saturated with one or other of the salts. The only fully saturated solution is at point  $A$ .

So far the composition of the complex has also given us the composition of the solution because the complex was all liquid. When the complex is within a field representing both solid and liquid it is necessary to determine the composition of both solution and solid and

the proportions of each. Point 4 is within such a heterogeneous field, and its composition is :

sodium nitrate . . . . .	70%
potassium nitrate . . . . .	6%
water . . . . .	24%

but this is partly liquid and partly solid. The composition of the solid is known, this being sodium nitrate.

It must be remembered that the composition of the complex does not alter, since nothing is added or taken away, but the composition of the liquid is different from that of the complex in the sense of having lost some sodium nitrate. The composition of the liquid therefore, lies on a straight line joining the complex (point 4) to  $\text{NaNO}_3$ , and it is on that part of the line *away from*  $\text{NaNO}_3$  because the sodium nitrate has been *removed from* the liquid. This is shown on the diagram by the dotted line joining point 4 to  $\text{NaNO}_3$ , this line being produced beyond 4 to meet the curve  $LA$  at  $x$ . The point  $x$  gives the composition of the solution which is seen to be :

sodium nitrate . . . . .	48.5%
potassium nitrate . . . . .	10.0%
water . . . . .	41.5%
	<hr/>
	100.0%

Having established the composition of the liquid and of the solid in a complex at the point 4, it remains to determine the *amount* of solid and liquid. As much which follows is based on the method now to be described, part of Fig. 9 has been reproduced on a larger scale in Fig. 10.

The distance between  $x$  and  $\text{NaNO}_3$  is divided into two parts by the point 4. The distance between  $x$  and 4 represents solid and the distance between  $\text{NaNO}_3$  and 4 represents liquid. It will be noticed that the divisions of the line representing solid and liquid are reversed in their proximity to the solid and liquid which they represent. Thus the length between  $x$  and 4 is near the liquid but represents solid. This is obvious when it is realized that as a complex approaches nearer to the liquid the amount of solid becomes less and less until it eventually disappears when the complex coincides with  $x$ .

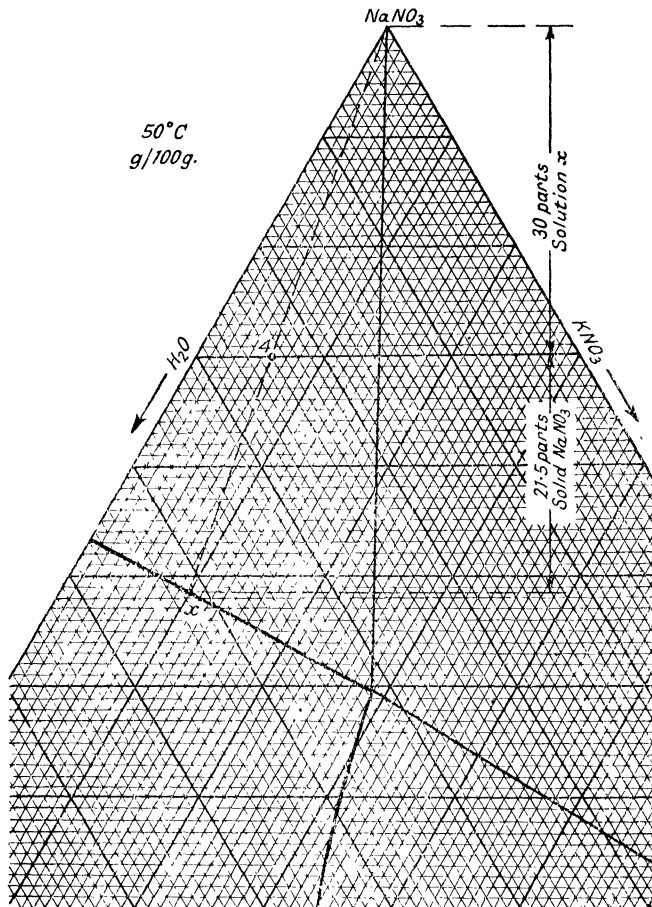
The distances under consideration can be measured by inspection in terms of the scale of the diagram. This is demonstrated in Fig. 10 and the distances are marked on the diagram. These are :

$x$ to 4 . . . . .	21.5 units of solid
$\text{NaNO}_3$ to 4 . . . . .	30.0 units of liquid
	<hr/>
total. . . . .	51.5 units of complex.

The above figures are brought to percentages by proportion :

51.5 parts of complex contain	21.5 parts solid,	30 parts liquid
100    "    "    "    "    "	41.7    "    "    "	58.3 parts liquid.

In the absence of a lattice on the diagram the distances may be measured on any convenient scale as it is the proportion only that is required.

FIG. 10.— $\text{NaNO}_3$ . $\text{KNO}_3$ .water. Corner of Fig. 9.

To summarize the data which has been deduced about the complex at the point 4 :

100 parts by weight of complex of composition :

sodium nitrate . . . . .	70.0%
potassium nitrate . . . . .	6.0%
water . . . . .	24.0%

will at 50° C. result in

solid sodium nitrate . . . . .	41.7 parts by weight
liquid . . . . .	58.3 parts by weight

the composition of liquid being :

sodium nitrate . . . .	48.5%
potassium nitrate . . . .	10.0%
water . . . . .	41.5%

In drawing the line from point 4 to  $\text{NaNO}_3$  and in the subsequent treatment use was made of a *general rule* which may now be stated.

*When any solid, liquid, or solution is added to a complex the point moves in a straight line towards that which is added.* Conversely, with *removal* it moves in a straight line *away from* that which is removed.

For example, if water is added to a complex at point 2, Fig. 9, the composition of the resulting complex will be somewhere on the straight line between the point 2 and  $\text{H}_2\text{O}$ . If, on the other hand, water is removed, then the resulting complex will be on a continuation of the same line, but in this case it will be on the side of point 2 *away from* the water.

Applying this rule to the examination of a complex made up of both liquid and solid we can determine the composition of the unknown part. Thus, if the solid is known, then the composition of the liquid is determined in the manner described for point 4. Conversely, if the composition of the liquid is known, then the solid can be determined, and an example of this is given later when discussing point 6.

The point 5 in Fig. 9 is analogous to point 4 except that for point 5 the solid phase is potassium nitrate instead of sodium nitrate. Thus  $\text{KNO}_3$  is joined by a straight line to the point 5 and the line is produced to cut the curve *MA* at *y*. The distance along this line, representing solid (*y* to 5) is 27 units, and the distance representing liquid ( $\text{KNO}_3$  to 5) is 40 units, the total being 67 units. Therefore 100 parts of complex contain

$$\frac{100 \times 27}{67} = 40.3 \text{ parts potassium nitrate}$$

and 59.7 parts of liquid of composition represented by the point *y*.

Summarizing :

100 parts of complex of composition (point 5) :

sodium nitrate . . . .	16.0%
potassium nitrate . . . .	60.0%
water . . . . .	24.0%

will at 50°C. result in

solid potassium nitrate . . . .	40.3 parts
liquid . . . . .	59.7 parts

---

100

the composition of liquid being (point *y*)

sodium nitrate . . . .	27.0%
potassium nitrate . . . .	33.0%
water . . . . .	40.0%.

Whereas for points 4 and 5 the solid was known, for point 6 it is the liquid which is known, the solid being a mixture of sodium nitrate and potassium nitrate. The problem, therefore, in this case, is to determine the composition of the solid. The same method is

used as for points 4 and 5, but the line is drawn from the known solution, point *A*, through the complex, point 6, instead of from the known solid. This line is produced *away from A* (because *A* is removed from the solid part) to meet the right-hand outside edge of the triangle at *z*. The proportion of liquid and solid is determined by measuring the distances between *z* and 6, this representing liquid, and between *A* and 6, this representing solid. In Fig. 9 these distances are :

$$\begin{array}{l} A \text{ to } 6 = 19.5 \text{ units of solid} \\ z \text{ to } 6 = 12.0 \text{ units of liquid} \\ \hline \text{in } 31.5 \text{ units of complex,} \end{array}$$

therefore 100 parts of complex contain 62.0 parts of solid and 38.0 parts of liquid. The composition of the liquid is read on the diagram at *A* and the composition of the solid is seen at a glance at *z*.

Summarizing :

100 parts of complex of composition (point 6)					
sodium nitrate	.	.	.	.	47.0%
potassium nitrate	.	.	.	.	41.0%
water	.	.	.	.	12.0%
will at 50° C. result in					
liquid	.	.	.	.	38.0 parts
solid	.	.	.	.	62.0 parts
					<hr/>
					100

the composition of liquid being (point <i>A</i> )					
sodium nitrate	.	.	.	.	39.8%
potassium nitrate	.	.	.	.	28.9%
water	.	.	.	.	31.3%

and the composition of solid being (point <i>z</i> )					
sodium nitrate	.	.	.	.	51.5%
potassium nitrate	.	.	.	.	48.5%
water	.	.	.	.	<i>nil</i> .

### The Interpretation of a Diagram with Double Salts (Intermediate Compounds).

The simple diagram so far studied concerns cases where no combination takes place between the two salts, the only solids being the components, either in the pure state or as a mixture. In some cases the two salts combine to form definite compounds or double salts. For example, under certain conditions potassium sulphate and sodium sulphate combine to form *glaserite*,  $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ , a compound containing 78.6% potassium sulphate and 21.4% sodium sulphate. This is a definite compound and not just a mixture. In the simple case there are only two fields where pure substance is in contact with solution. With the formation of a double salt a third field containing a pure substance makes its appearance, in this case the field of glaserite and solution. It will be easier to consider this by passing directly to the diagram.

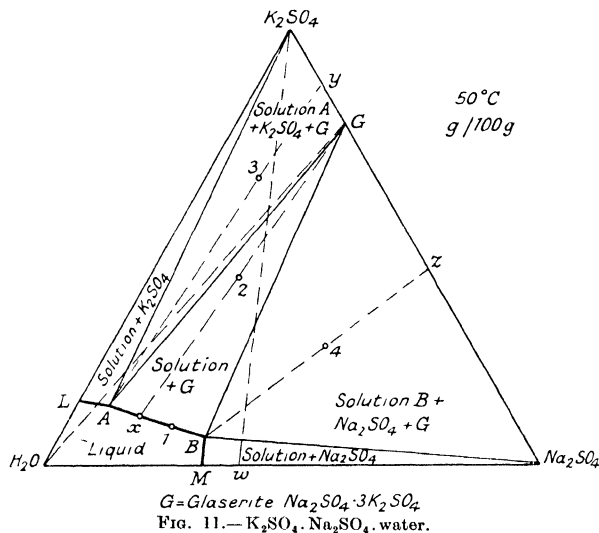


TABLE 10  
SODIUM SULPHATE.POTASSIUM SULPHATE.WATER  
(From E. Cornec and H. Krombach, *Caliche*, 1928)  
Composition of saturated solutions at 50° C.

Ref. Letter.	K <sub>2</sub> SO <sub>4</sub> . %	Na <sub>2</sub> SO <sub>4</sub> . %	Water. %	Solid Phase
<i>L</i> . . . .	14.19	0	85.81	K <sub>2</sub> SO <sub>4</sub>
<i>A</i> . . . .	13.8	5.68	80.52	K <sub>2</sub> SO <sub>4</sub> + Glaserite
<i>B</i> . . . .	5.85	29.4	64.75	Na <sub>2</sub> SO <sub>4</sub> + Glaserite
<i>M</i> . . . .	0	31.6	68.4	Na <sub>2</sub> SO <sub>4</sub>

Glaserite is 3K<sub>2</sub>SO<sub>4</sub>.Na<sub>2</sub>SO<sub>4</sub> and contains 78.6% K<sub>2</sub>SO<sub>4</sub>, 21.4% Na<sub>2</sub>SO<sub>4</sub>.

Table 10 gives the figures for plotting the diagram for potassium sulphate, sodium sulphate and water at 50°C., and Fig. 11 is the diagram. Although a third salt, glaserite, has been introduced the system is still one of three components, two salts and water, because



any point in the diagram can be expressed in terms of the two simple sulphates and water, as seen in Table 10. The reader should compare Fig. 11 with Fig. 9. The difference is that instead of one point *A* we have two similar points *A* and *B* with a curve between them. The liquid field, bounded by the lines and curves between H<sub>2</sub>O, *L*, *A*, *B* and *M*, and the two fields marked "solution + K<sub>2</sub>SO<sub>4</sub>" and "solution + Na<sub>2</sub>SO<sub>4</sub>" are similar in all respects to those already considered in the case of Fig. 9 and may be examined both qualitatively and quantitatively in the manner already described.

The additional fields in Fig. 11 are defined by first marking the composition of glaserite by a point on the line between potassium sulphate and sodium sulphate. The points *A* and

*B* are then joined by straight lines to the point for glaserite. Any complex within the resulting field bounded by the lines joining *A* and *B* to glaserite contains solid glaserite and a solution, the solution being somewhere on the curve *AB*.

Apart from the liquid field the diagram has now been divided into five fields. Three of these fields, as already mentioned, represent a pure salt in equilibrium with a solution. The remaining two fields represent a solution of fixed composition, *A* or *B*, with a mixed solid phase of potassium sulphate plus glaserite or sodium sulphate plus glaserite. The introduction of the extra field for solution plus solid glaserite has divided the mixed solids field into two parts. There is now no field with solution plus a mixture of potassium sulphate and sodium sulphate, meaning that it is not possible for solid potassium sulphate and solid sodium sulphate to exist together in equilibrium with a solution.

**QUANTITATIVE.** For a quantitative examination we propose to confine ourselves in this case to the three new fields, those containing glaserite.

Point *A* represents a solution similar to point *L* and to points on the curve *LA* in that the solution is saturated with potassium sulphate, but at *A* it is also saturated with glaserite. In the same way point *B* represents a solution saturated with sodium sulphate and glaserite.

A point on the curve *AB*, such as point 1, represents a solution saturated with glaserite. It contains both potassium sulphate and sodium sulphate in solution, but it is not *saturated* as to either. This means that if glaserite is added it will not dissolve; but if potassium sulphate or sodium sulphate is added they will dissolve, moving point 1 towards *A* in one case and towards *B* in the other. Since glaserite itself is a compound of potassium sulphate and sodium sulphate it is usual to express the composition of all *solutions* in terms of potassium sulphate and sodium sulphate and not in terms of glaserite. Thus the composition at point 1 is seen to be:

potassium sulphate . . . .	8.0%
sodium sulphate . . . .	21.0%
water . . . .	71.0%

If it is desired to express this composition in terms of glaserite the potassium sulphate is calculated into glaserite by multiplying by  $\frac{100}{78.6}$ , giving 10.17%. Thus 2.17% sodium sulphate is present as glaserite leaving 18.83% sodium sulphate in excess. So that point 1 may be regarded as composed of:

glaserite . . . .	10.17%
sodium sulphate . . . .	18.83%
water . . . .	71.00%
	<hr/>
	100.00%

Point 2 represents a complex within the glaserite field. Applying the general rule to find the composition of the solution a straight line is drawn from *G* and through the point 2 to meet the curve *AB* at *x*. In the example taken the composition of the solution is:

potassium sulphate . . . .	11.0%
sodium sulphate . . . .	13.0%
water . . . .	76.0%

The relative amounts of solution and solid are determined by the method described on page 33. That is, the distance from  $G$  to 2 represents solution, whereas the distance  $x$  to 2 represents solid. Measuring along the scale of the lattice these distances are :

$G$  to 2 = 41 units representing solution

2 to  $x$  = 35 units representing solid

total 76 units representing complex.

Therefore 100 parts by weight of complex (point 2)  
contain 54.0 parts by weight of solution (point  $x$ )  
and 46.0 parts by weight of solid (glaserite).

Point 3 represents a complex in a field of mixed solids and solution, the two solids being potassium sulphate and glaserite. The composition of the solution is seen at a glance, being represented by the point  $A$ . The composition of the solid is found by drawing a line from the point of known liquid,  $A$ , through point 3 to meet the right-hand outside edge of the triangle at  $y$ . The point  $y$  then indicates the composition of the mixed solids. This is usually expressed in terms of potassium sulphate and sodium sulphate :

potassium sulphate . . .	88%
sodium sulphate . . .	12%

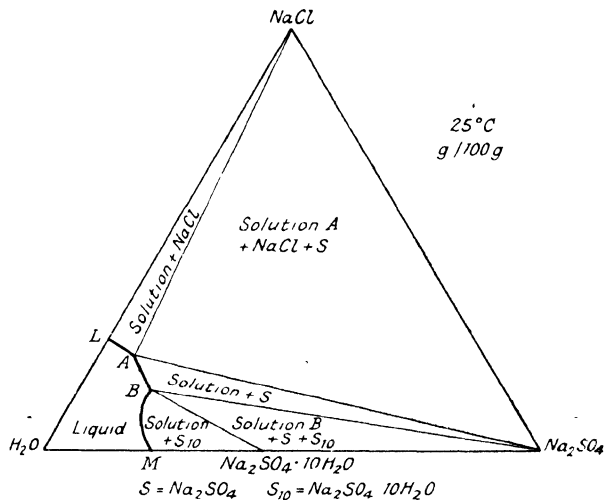
but it must be noted that there is no free sodium sulphate, all the sodium sulphate being present as glaserite.

The proportion of liquid and solid is determined by measuring the distances between  $y$  and 3 (representing liquid) and between  $A$  and 3 (representing solid). These are 25.0 and 55.52 units of the lattice respectively.

Point 4 is treated in a way exactly similar to that for point 3, the solution being at  $B$  and the mixed solids being represented at  $z$ , a mixture of glaserite and sodium sulphate.

The system just studied includes an example of a solution which has the same composition as the double salt but which is not in equilibrium with it. W. Meyerhoffer, 1897, refers to this as an *incongruently saturated solution*. In Fig. 11 a mixture of glaserite, with just sufficient water to dissolve it, gives a saturated solution represented by the point where the straight line from glaserite to  $H_2O$  cuts the curve  $LA$ . This solution is incongruent because the only solid phase with which it could be in equilibrium is not glaserite but potassium sulphate. With slightly less water the solution point would move towards  $A$  but the solid phase would still be potassium sulphate. With still less water the solution would remain at  $A$  while the solid phase moved from  $K_2SO_4$  towards glaserite, only becoming glaserite when there was no water. Conversely, the least drop of water decomposes glaserite into a mixture of glaserite and potassium sulphate. This use of the word incongruent should be compared with its similar use on p. 16 and later on p. 102.

**The Interpretation of a Diagram with Hydrate.** When one of the salts of a three-component system forms a hydrate there are two possibilities : the anhydrous salt may disappear completely from the system or both hydrated and anhydrous salt may be found in different parts of the system. By taking sodium sulphate as an example both cases may be illustrated. Sodium sulphate combines with water to form the decahydrate,  $Na_2SO_4 \cdot 10H_2O$ , commonly known as Glauber's salt. In equilibrium with water and sodium chloride the anhydrous sulphate is completely absent at  $17.5^\circ C$ . At  $25^\circ C$ ., on the other hand, both the decahydrate and the anhydrous sulphate are found. Tables 11 and 12

FIG. 12.—NaCl. Na<sub>2</sub>SO<sub>4</sub>. water.

give the data for these two systems. Table 11, at 25° C., will be taken first and Fig. 12 is the diagram.

TABLE 11  
SODIUM CHLORIDE-SODIUM SULPHATE-WATER  
(From A. Chretien, *Caliche*, 1926)  
Composition of saturated solutions at 25° C.

Ref. Letter.	NaCl. %	Na <sub>2</sub> SO <sub>4</sub> %	Water. %	Solid Phase.
<i>M</i> . . . .	0	21.6	78.4	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O
	7.66	16.0	76.4	
<i>B</i> . . . .	14.5	14.5	71.1	Na <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O
	18.4	10.4	71.2	Na <sub>2</sub> SO <sub>4</sub>
<i>A</i> . . . .	22.7	7.1	70.2	Na <sub>2</sub> SO <sub>4</sub> + NaCl
	24.6	3.35	72.0	NaCl
<i>L</i> . . . .	26.6	0	73.4	"

Na<sub>2</sub>SO<sub>4</sub> · 10H<sub>2</sub>O = 44.4% Na<sub>2</sub>SO<sub>4</sub>, 55.9% H<sub>2</sub>O.

TABLE 12  
SODIUM CHLORIDE-SODIUM SULPHATE-WATER  
(From A. Chretien, *Caliche*, 1926)  
Composition of saturated solutions at 17.5° C.

Ref. Letter	Na <sub>2</sub> SO <sub>4</sub> %	NaCl %	Water %	Solid Phase
<i>M</i> . . . .	13.8	0	82.6	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O
	8.51	8.12	83.4	"
	6.8	16.9	76.3	"
<i>A</i> . . . .	7.38	22.3	70.3	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O + NaCl
<i>L</i> . . . .	0	26.5	73.5	NaCl

In this diagram there is a possibility of three different salts being obtained in the solid state, sodium chloride, sodium sulphate decahydrate and anhydrous sodium sulphate. This compares with Fig. 11 and there are the same number of fields, six, in each case. The only difference is that the extra compound, in this case the decahydrate, is represented by a point on the edge between water and sodium sulphate instead of being between the two salts.

The four fields marked "liquid," "solution + NaCl," "solution + *S*" and "solution *A* + NaCl + *S*" are so similar to previous examples that no further explanation is required. On the diagram  $\text{NaSO}_4$  is marked *S* and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is marked *S*10 for convenience.

In the field marked "solution + *S*10" any complex will contain a saturated solution of the decahydrate and some solid decahydrate. Such a complex is examined in the usual

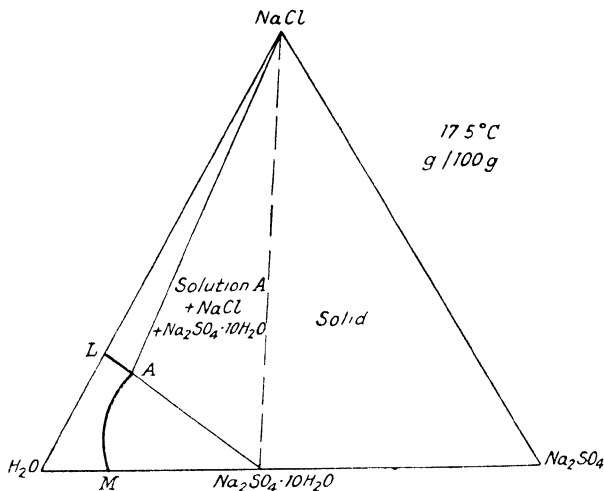


FIG. 13.— $\text{NaCl} \cdot \text{Na}_2\text{SO}_4$  water.

way by drawing a line from the point of known solid,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , through the complex to meet the curve *BM*. The ratio of the two parts of this line then gives the proportion of solid decahydrate to solution.

In the remaining field, marked "solution *B* + *S* + *S*10," any complex will contain a solution of composition *B* and a mixture of the two solids, anhydrous and decahydrate. The solution *B* is saturated with respect to both of these compounds, implying that it is incapable of dissolving any more of either of them. The proportion and amount of the two solids is determined by applying the general rule of drawing a straight line from the point *B*, of known solution, through the complex to meet the edge of the triangle between  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$ . Where this line meets the edge of the triangle is the composition of the mixed solids being expressed in terms of sodium sulphate and water, remembering, however, that the water content is really present in combination with some of the sodium sulphate as decahydrate. For this latter reason it may sometimes be necessary to express the composition in terms of anhydrous and hydrate. This is done by calculating the amount of sodium sulphate which will combine with the amount of water found.

Fig. 13 is the diagram, plotted from Table 12, showing that, at  $17.5^{\circ}\text{C}$ ., the anhydrous field found in Fig. 12 has disappeared. The peculiarity about this diagram is that after plotting the curves and drawing the lines in the manner hitherto described one is left with a quadrilateral area between  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $A$ . To complete the diagram this area must be divided into two triangular fields by the line joining  $\text{NaCl}$  to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

Any complex within the field marked "solution  $A + \text{NaCl} + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ " contains a solution of known composition,  $A$ , and a mixture of the two solids, sodium chloride and Glauber's salt. Solution  $A$  is saturated with respect to these two salts. In ascertaining the composition of the mixed solids the line drawn from  $A$  through the complex must be produced only as far as the line joining  $\text{NaCl}$  to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . The point obtained on this line gives directly the proportion of sodium chloride and Glauber's salt.

The field marked "solid" introduces a new aspect; any complex within this field contains no liquid, being a mixture of the three solids, sodium chloride, sodium sulphate anhydrous and sodium sulphate decahydrate. This may cause the reader to object to the earlier statements which said that the anhydrous salt had completely disappeared. That statement was meant to imply that the field of the pure anhydrous salt had disappeared.

The remaining fields of Fig. 13 are so much like those already examined that no further details are given here.

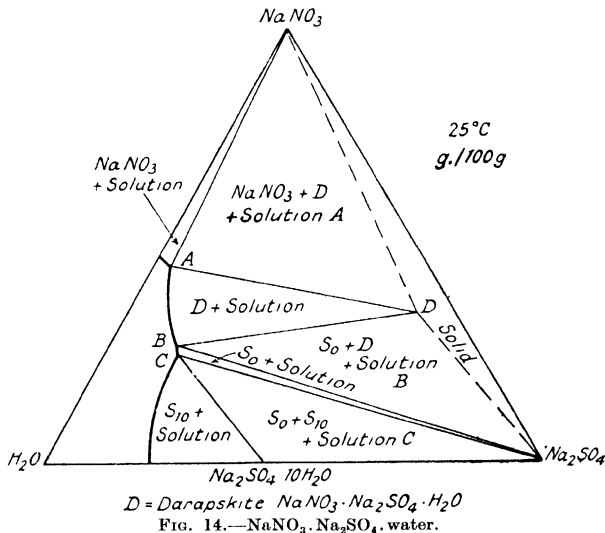


FIG. 14.— $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , water.

**A More Complicated Diagram.** Table 13 contains figures for the system sodium nitrate, sodium sulphate and water at  $25^{\circ}\text{C}$ ., and Fig. 14 is the phase diagram plotted from this data.

It is not proposed to deal with this in detail as the composition of each field is marked on the diagram. Thus there is a simple hydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . There is a double salt, but in this case the double salt is also a hydrate,  $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (darapskite). There is also a solid field containing sodium nitrate, sodium sulphate and darapskite.

TABLE 13  
SODIUM NITRATE.SODIUM SULPHATE.WATER  
(From A. Chretien, *Caliche*, 1926)  
Composition of saturated solutions at 25° C.

NaNO <sub>3</sub> . %	Na <sub>2</sub> SO <sub>4</sub> . %	Solid Phase
47.9	0	NaNO <sub>3</sub>
46.5	1.57	"
45.2	3.05	NaNO <sub>3</sub> + Darapskite
44.6	3.40	Darapskite
43.1	3.74	"
37.7	6.17	"
31.1	10.2	"
29.5	11.3	"
27.7	12.7	"
26.8	13.4	Darapskite + Na <sub>2</sub> SO <sub>4</sub>
25.0	14.6	Na <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O
21.2	14.8	Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O
12.6	16.5	"
0	21.6	"

Darapskite is NaNO<sub>3</sub>.Na<sub>2</sub>SO<sub>4</sub>.H<sub>2</sub>O and contains 34.6% NaNO<sub>3</sub>, 58.0% Na<sub>2</sub>SO<sub>4</sub>, 7.4% H<sub>2</sub>O.

**Acids and Bases instead of Salts.** Thus far the mixtures considered have been of two salts and water. The same methods are applicable when, instead of salts, the two "substances" are acid and base, as, for example, calcium oxide (CaO) and phosphorus

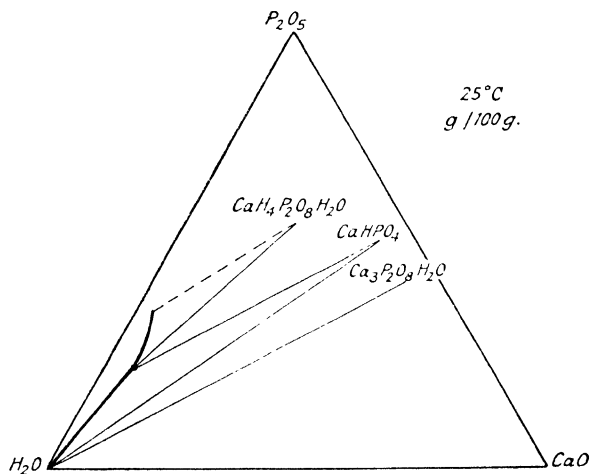


FIG. 15.—P<sub>2</sub>O<sub>5</sub>.CaO.water.

pentoxide (P<sub>2</sub>O<sub>5</sub>). Table 14 gives the figures for calcium oxide and phosphorus pentoxide and Fig. 15 is the diagram. The data given is not complete but is sufficient to illustrate this type of diagram.

TABLE 14  
 PHOSPHORIC ANHYDRIDE-CALCIUM OXIDE-WATER  
 (Adapted from H. Bassett, *Z. anorg. Chem.*, 1908, **59**, 1-55)  
 Composition of saturated solutions at 25° C.

P <sub>2</sub> O <sub>5</sub> , %	CaO, %	Solid Phase.
36.11	3.09	CaH <sub>4</sub> P <sub>2</sub> O <sub>8</sub> ·H <sub>2</sub> O
31.97	4.12	"
28.34	4.91	"
27.99	4.93	"
25.45	5.49	"
22.90	5.52	CaHPO <sub>4</sub>
17.55	4.50	"
15.34	4.03	"
9.10	2.64	"
6.05	1.88	"
3.61	1.18	"
2.39	0.83	"
0.09	0.04	Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> ·H <sub>2</sub> O
0.05	0.02	"

CaH<sub>4</sub>P<sub>2</sub>O<sub>8</sub>·H<sub>2</sub>O contains 56.4% P<sub>2</sub>O<sub>5</sub>, 22.2% CaO.  
 CaHPO<sub>4</sub> " 52.2% P<sub>2</sub>O<sub>5</sub>, 41.1% CaO.  
 Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub>·H<sub>2</sub>O " 43.3% P<sub>2</sub>O<sub>5</sub>, 51.2% CaO.

In a case such as this there is always at least one intermediate compound, not a double salt as already encountered, but a compound of the two radicals. With calcium oxide and phosphorus pentoxide there are three well-known intermediate compounds, tricalcium phosphate (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O), calcium phosphate (CaHPO<sub>4</sub>), and acid calcium phosphate (Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O). It is because of this type of diagram that it is preferred to use the term intermediate compound rather than double salt. Thus in Fig. 13 glaserite was an intermediate compound.

The diagram is interpreted in the usual way, remembering that all compositions are in terms of calcium oxide and phosphorus pentoxide.

It will be noticed that the field of tricalcium phosphate and solution is so narrow that it can only be represented by a line on the diagram instead of the usual triangular area. Likewise the field for calcium hydroxide is also represented by a line only and this line lies on the bottom edge of the diagram.

In the upper part of the diagram the curve is incomplete. If it could be completed the curve would meet the left-hand edge of the triangle at a point representing the solubility of phosphorus pentoxide in water at 25° C.

In practice interest is usually centred around the intermediate compounds and it is not then necessary to know how the curves meet the edges of the triangle. In any case it is often very difficult to obtain the data experimentally for the extremities.



## CHAPTER VI

### PRACTICAL APPLICATION OF THREE-COMPONENT DIAGRAM

The most frequent application of three-component diagrams is for the production of a salt in a pure state. From the previous chapter it will be realized that to achieve such an object a complex must ultimately be obtained within the field of the salt required. This salt may be one of the two main salts of the diagram or a hydrate of one of them or a double compound of the two salts, which might itself be a hydrate. If the complex does not naturally lie within the correct field, then one or more operations must be performed to cause it to move into that field. The means available for bringing about such a change are :

- (a) removing water (evaporation),
- (b) adding water (dilution),
- (c) adding one of the salts (but naturally never the one required),
- (d) altering the temperature.

In complicated cases several of these operations may be combined. The removal or addition of water or the addition of one of the salts moves the position of the complex on the diagram. On the other hand, change of temperature does not alter the position of the complex but changes the configuration of the diagram so that a given field may be altered to embrace the complex.

Before proceeding to study the effects of the above four operations it is necessary to understand something of the nature of precipitation.

**Precipitation.** As an example of precipitation suppose calcium acid phosphate,  $\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$  is to be prepared. It might appear at first that the method would be to add the chemical equivalent of lime to a solution of phosphoric acid. A mere glance at the three-component diagram is sufficient to show that such proportions will not precipitate the desired compound.

The diagram required has already been given, Fig. 15. This shows that calcium acid phosphate when precipitated will be in the form of its monohydrate, having the following composition :

CaO	.	.	.	22.2%
$\text{P}_2\text{O}_5$	.	.	.	56.4%
water	.	.	.	21.4%

If lime and phosphoric acid are taken in the proportions to form calcium acid phosphate then, no matter how much water is present, the mixture (complex) will be somewhere on the straight line joining the point water to the point marked  $\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$ . No part of this line lies within the field of solid  $\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$  and solution. It is, therefore, impossible to take such a complex and obtain precipitated calcium acid phosphate. The actual result would be for neutral calcium phosphate,  $\text{CaHPO}_4$ , to be precipitated, while the solution would be enriched in phosphoric acid.

The only way to precipitate calcium acid phosphate is to have less lime than the chemical equivalent so that the complex may come within the field  $\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O} + \text{solution}$ .

In a similar way double salts (intermediate compounds such as darapskite

( $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ) cannot generally be prepared by mixing the two salts in stoichiometrical proportions. It is usually necessary to have one or the other in excess. For example, Fig. 14 shows that to prepare darapskite there must be an excess of sodium nitrate.

**Evaporation and Dilution.** To revert to the methods used for moving a complex into the desired field evaporation and dilution will be considered first. On removing water, e.g. by evaporation, the composition of the complex moves in a straight line on the diagram *away from* the corner marked  $\text{H}_2\text{O}$ . On the other hand, on adding water to a complex the composition of the complex moves in a straight line on the diagram *towards* the corner marked  $\text{H}_2\text{O}$ . It is, therefore, an easy matter to see whether adjustment of the water content will bring the complex within the required field or not.

As an example, take the case of sodium nitrate and potassium nitrate at  $50^\circ \text{C}$ ., Fig. 9. Suppose the original complex is a solution containing 10% sodium nitrate and 30% potassium nitrate. This solution on evaporation of water will give potassium nitrate in the solid phase because a straight line from the corner  $\text{H}_2\text{O}$  to the complex, when produced, passes into the potassium nitrate field.

In order to obtain as high a yield of solid potassium nitrate as possible the solution may be evaporated until the complex reaches the point where the *line of evaporation* meets the line joining *A* to  $\text{KNO}_3$ . This complex will be seen on inspection to be 21% sodium nitrate, 63% potassium nitrate and 16% water, some of the potassium nitrate being present as solid. If evaporation is carried beyond this point a mixture of sodium nitrate and potassium nitrate will be obtained.

To take another example, of the opposite kind, suppose the original complex is a mixture of solids and liquid containing 30% sodium nitrate and 60% potassium nitrate. It is required to obtain pure potassium nitrate. An inspection of the diagram (assuming a temperature of  $50^\circ \text{C}$ .) shows that the original complex contains both sodium nitrate and potassium nitrate in the solid phase. The effect of dilution is seen by drawing a straight line from the complex to  $\text{H}_2\text{O}$ . This line passes through the potassium nitrate field so that by adding sufficient water to bring the complex within this field pure potassium nitrate can be obtained. Actually what happens is that the added water dissolves all the sodium nitrate but only part of the potassium nitrate.

The maximum yield of potassium nitrate will be obtained if only just sufficient water is added to bring the complex to the point where the *line of dilution* cuts the line joining *A* to potassium nitrate. This is where the complex has the composition 26% sodium nitrate, 53% potassium nitrate, and 22% water.

To summarize: the effect of evaporation and dilution may be seen on a diagram by drawing a straight line from the corner representing water through the complex under consideration. With evaporation the complex moves along this line *away from* water; with dilution it moves along the line *towards* water.

In the examples given the complex was such that the evaporation—dilution line passed through the required field. If this had not been so then a simple operation of dilution or evaporation would not be sufficient to give solid potassium nitrate. We shall revert to this later.

An example of the phase reactions which take place during the removal of water without change of temperature will now be considered in detail using Fig. 9. The complex, which is an unsaturated solution, is represented by the point *a*. During the removal of water the point representing the complex moves from *a* towards the curve *MA*, and when

it reaches this curve the complex is a solution saturated as to  $\text{KNO}_3$  and the solid phase  $\text{KNO}_3$  may be considered as just having appeared.

The system has gained a phase, so it has lost a degree of freedom. Thus, during the further removal of water, the composition of the solution is fixed by nature as some point on the curve  $MA$ . (See page 35, point 5.)

The further removal of water now causes the composition of the complex to move in the same straight line from the curve towards  $b$ , during which time the point representing the solution, saturated as to  $\text{KNO}_3$ , but not saturated as to  $\text{NaNO}_3$ , moves along the curve towards  $A$ . During this period of change the solid phase is  $\text{KNO}_3$  in equilibrium with a solution of varying composition along part of the curve  $MA$ . When the composition of the complex arrives at  $b$  the composition of the solution is at  $A$  and is saturated as to both salts.

This system has now gained another phase and so lost another degree of freedom, and with the further removal of water the composition of the solution cannot change.

If the removal of water is continued the composition of the solution will be unchanged. The composition of the complex will continue to move along the line  $\text{H}_2\text{O}-d$  and, after leaving  $b$ , will be at a point on the line between  $b$  and  $d$ . A line drawn from  $A$  through this point between  $b$  and  $d$  will meet the  $\text{NaNO}_3-\text{KNO}_3$  side of the triangle somewhere between  $d$  and  $\text{KNO}_3$  and will represent the composition of the mixed solid phase at that stage of the evaporation. The composition of the mixed solids being deposited, while water is being removed from solution  $A$ , is represented by  $c$  on the side of the triangle and  $c$  represents the same composition as  $A$  dried up.

The composition of the mixed solids deposited during the *whole* of the evaporation of the solution represented by  $a$  will be found at  $d$ . Thus  $A$  is the drying-up point of the system at  $50^\circ\text{C}$ ., and any solution point in the liquid field or on either of the curves will move along one of the curves to  $A$  if sufficient water is removed. Further evaporation will cause the solution to dry up at composition  $A$ . This means that down to the last trace the liquid has composition  $A$  but the solid deposited has composition  $c$ .

The addition of water to the solid complex  $d$ , at  $50^\circ\text{C}$ ., would have resulted in the same phase reaction but in the reverse order. The removal of water causes the composition of solutions to move along the curve towards the isothermal invariant point, and it is usual to denote this by arrow heads on the curves. The reason for this will be evident at a later stage.

The phase reactions caused by the isothermal removal of water from a complex which can form a double salt is somewhat different from the simple case just considered. Fig. 11 which has already been studied is the isotherm at  $50^\circ\text{C}$ . representing  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  and water. If a line is drawn from  $G$ , which represents the composition of glaserite, to water, it will be noticed that the invariant points  $A$  and  $B$  are both on the same side of this line and are in the triangle  $\text{H}_2\text{O}-G-\text{Na}_2\text{SO}_4$ .

The point  $B$  represents a solution saturated as to  $\text{Na}_2\text{SO}_4$  and glaserite and the solution may be represented in terms of these two salts and water. The solution is, therefore, said to be congruently saturated. The point  $A$ , on the other hand, is saturated as to  $\text{K}_2\text{SO}_4$  and glaserite and cannot be represented in positive terms of  $\text{K}_2\text{SO}_4$ , glaserite and water; this solution is incongruently saturated. In other words, the line drawn from glaserite to water does not cut the curve  $AB$  representing solutions saturated as to glaserite, so glaserite is decomposed by water.

If sufficient water is added to glaserite the complex would be an unsaturated solution, that is, a point on the line from  $\text{H}_2\text{O}$  to  $G$  but within the all-liquid field. If water is

evaporated from this solution without change of temperature the point representing the complex will move towards the curve  $LA$  and, on meeting the curve, the solution will be saturated as to  $K_2SO_4$  only.

If the evaporation is continued the point representing the complex will move still nearer to  $G$  and will cut the line from  $A$  to  $K_2SO_4$  during which time the solution point will have moved to  $A$ , while  $K_2SO_4$  was being deposited as the solid phase.

When the solution point is at  $A$  a new phase, glaserite, has just appeared, and on the further evaporation of water the solution will remain at  $A$ ,  $K_2SO_4$  will dissolve and glaserite will be deposited. This will continue until all the  $K_2SO_4$  has been converted to glaserite and the solution will dry up at composition  $A$ . The solid phase becomes all glaserite only when solution  $A$  has dried up. The point  $A$  is the drying-up point of all solutions within the system  $K_2SO_4$ -glaserite-water.

The unsaturated solution which has just been considered was represented by a point on the line from the water corner to  $G$ . If a small amount of  $Na_2SO_4$  was added to this solution it would be represented by a point still within the all-liquid field. The removal of water from this solution will cause the point representing the complex to move along a new line, a line from  $H_2O$  through the new point and produced to meet the  $K_2SO_4$ - $Na_2SO_4$  side of the figure at a point near  $G$  but on the  $Na_2SO_4$  side of it. When the point representing the complex meets the curve  $LA$  the solution is saturated as to  $K_2SO_4$  and the removal of more water causes the point representing the complex to cross the  $K_2SO_4$  field and meet the line  $K_2SO_4$ - $A$ . During this time the point representing the solution has moved along the curve  $LA$  to  $A$ , and  $K_2SO_4$  has been deposited as solid phase.

At the point  $A$  a new solid phase, glaserite, appears, so the system, i.e. the complex, has lost a degree of freedom and the solution must remain at  $A$  as long as there are two solid phases present. The continued removal of water causes the  $K_2SO_4$  to dissolve and glaserite to be deposited. The point representing the complex crosses the mixed field of  $K_2SO_4$  and glaserite,  $K_2SO_4$  dissolves, glaserite is deposited and the composition of the solution remains at  $A$ . This statement may be proved geometrically on the diagram by drawing a line from  $H_2O$  through  $A$  and producing to a point within the figure to represent the removal of water, then from the point selected by drawing a line towards  $K_2SO_4$  to represent the dissolving of  $K_2SO_4$ . This line will cut the line  $GA$  which represents the removal of glaserite. Thus from the point  $A$  water was removed,  $K_2SO_4$  added and glaserite removed without changing the position of  $A$ .

To return to solution  $A$ , when sufficient water has been removed all the  $K_2SO_4$  will have been converted to glaserite and, as the phase  $K_2SO_4$  has disappeared, a degree of freedom has been gained. On the removal of more water the solution point will move from  $A$  and along the curve towards  $B$ . The point representing the complex will cross the glaserite field during which time glaserite only is the solid phase. When the point representing the complex meets the line  $BG$  the solution will be at  $B$  and a new phase  $Na_2SO_4$  will have just appeared. Arrowheads, if shown on the curves, would lead to the point  $B$ , the congruently saturated drying-up point. The removal of still more water causes the point representing the complex to cross the mixed field of glaserite and  $Na_2SO_4$ , but solution  $B$  is unchanged in composition. The compositions of solution  $B$  and of the mixed solid phase being deposited, during this period of the evaporation, are the same. Solution  $B$  finally dries up at composition  $B$  and the total solids have the same composition as the original solution with water removed. The points  $A$  and  $B$  are both drying-up points but  $B$  is the final or system drying-up point.

An example of a hydrated double salt is given in Fig. 14, when the salt darapskite appears. A solid phase of this type, when encountered in a ternary system, is called a ternary compound because it can only be represented in terms of all three components. The point *A* represents a congruently saturated solution, *B* an incongruently saturated solution and the double salt darapskite is decomposed by water. The reader should find no difficulty in following the phase reactions when water is added to, or removed from, a complex represented on this figure.

Before leaving the question of dilution, attention must be called to a special kind of dilution which often occurs in practice, that is, dilution with another solution, or even with a solid. For example, on Fig. 9, if the complex 30% sodium nitrate, 60% potassium nitrate (point *e*) is diluted with a solution of potassium nitrate containing say 20%, the result of such dilution will be on the line joining the original complex point *e* to the point representing 20% potassium nitrate, 80% water.

**Addition of a Salt.** It will be obvious that dilution of a complex by *adding a solid salt* will move the complex along the line joining the original complex to the point representing the solid. The phase reactions caused by such addition will now be considered in detail, using Fig. 11. The complex represented by the point *w* is a system of one salt and water, a binary system, and these remarks apply also to a similar point on the  $\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  side of the triangle. If some  $\text{K}_2\text{SO}_4$  is added to complex *w*, the  $\text{K}_2\text{SO}_4$  dissolves and the point representing the solution will be on the curve *MB* and the system is no longer binary but ternary. As more  $\text{K}_2\text{SO}_4$  is added and time allowed for equilibrium, the point representing the solution will move along the curve towards *B* and will be at *B* when sufficient  $\text{K}_2\text{SO}_4$  has been added and the point representing the complex is on the line from *B* to  $\text{Na}_2\text{SO}_4$ . At *B* the solution is saturated as to  $\text{Na}_2\text{SO}_4$  and glaserite, the glaserite phase having just appeared. The system has gained a phase, so it has lost a degree of freedom and *B* is an isothermal invariant point.

If more and more  $\text{K}_2\text{SO}_4$  is added the point representing the complex moves nearer to  $\text{K}_2\text{SO}_4$  on the line *w*— $\text{K}_2\text{SO}_4$  and crosses the field of mixed solid phases,  $\text{Na}_2\text{SO}_4$  and glaserite, but the point representing the solution remains at *B*. During this time  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  are going into solution and glaserite is being deposited.

When the point representing the complex meets the line from *B* to glaserite the solution point is still *B*, but the solid  $\text{Na}_2\text{SO}_4$  may be considered as having just dissolved. The addition of more  $\text{K}_2\text{SO}_4$  now causes the point representing the solution to leave *B* and move along the curve *BA*. The system has lost a phase,  $\text{Na}_2\text{SO}_4$ , and therefore gained a degree of freedom, so, in addition to temperature, a concentration may be selected. While the solution point moves on the curve towards *A*, on the addition of more  $\text{K}_2\text{SO}_4$ , the point representing the complex crosses the glaserite field and the solid phase formed is all glaserite. When this point meets the line from *A* to glaserite the composition of the solution is at *A* and a new phase,  $\text{K}_2\text{SO}_4$ , has just appeared. The system has regained a phase, though not the same phase, and has therefore lost the degree of freedom it gained when the solution point left *B*.

The point *A* is an isothermal invariant point and solution *A* is saturated as to glaserite and  $\text{K}_2\text{SO}_4$ . The addition of more  $\text{K}_2\text{SO}_4$  will cause no further change in the composition of this solution.

Two examples of double salts in a ternary system have been given and some of their phase reactions have been studied. Before leaving this subject it should be mentioned that another type of double salt exists where the double salt is not decomposed by water.

These double salts may be anhydrous or hydrated, but their saturation curves lie in such a position that the line drawn from water to the composition of the double salt cuts the saturation curve and divides the ternary system into two other ternary systems. Each of these systems then contains a ternary invariant point congruently saturated as to double salt and one of the single salts. The dividing line becomes a binary system, the double salt and water, and the whole system contains three congruent drying-up points. An example of a hydrated double salt of this type is ammonium ferrous sulphate and an anhydrous example is in the system  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Li}_2\text{SO}_4$ -water at  $30^\circ\text{C}$ . (Schreinemakers, *Z. physik. Chem.*, 1907, **59**, 641.) The subject of double salts is an extensive one and it is possible here only to indicate some of their phase reactions.

**The Addition of a Salt to a System containing a Hydrate.** In Fig. 12, a solution represented by the point *M* is saturated as to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . It is a system of one salt and water, a binary system, and the same remarks apply to the solution represented by the point *L*.

If some  $\text{NaCl}$  is added to solution *M* the  $\text{NaCl}$  will dissolve and the solution will be represented by a point on the curve *MB* and the system is no longer binary but ternary.

If more and more  $\text{NaCl}$  is added and time allowed for equilibrium the point representing the solution will move along the curve *MB* and with the correct amount of salt added the point will be at *B*. The solution is then saturated as to Glauber's salt and anhydrous sodium sulphate and the complex is at a point within the mixed field, the triangle  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SO}_4 - \text{B}$ . The system has now gained a phase and has therefore lost a degree of freedom, and the composition of solution *B* is invariant for the temperature of  $25^\circ\text{C}$ .

The addition of more  $\text{NaCl}$ , even though it dissolves, does not change the composition of solution *B*, because Glauber's salt becomes dehydrated and  $\text{NaCl}$  dissolves, so the solution can be of the same composition so long as any Glauber's salt remains. When sufficient  $\text{NaCl}$  has been added and all the Glauber's salt has been dehydrated, then the dissolving of more salt causes the point, representing the solution, to leave *B* and move along the curve towards *A*. That is, the system loses a phase when all the Glauber's salt is dehydrated and therefore a degree of freedom is gained. If excess of  $\text{NaCl}$  is now added and time allowed for equilibrium, the point representing the solution will move to *A* when a new phase,  $\text{NaCl}$ , appears and the solution is again invariant.

**Altering the Temperature.** It has already been stated that whereas addition or removal of a substance moves the complex, change of temperature only changes the configuration of the fields. It is convenient when dealing with changes of temperature to have the diagrams of different temperatures on the same figure. Fig. 16 is an example of three such diagrams superimposed; the components are sodium nitrate, potassium nitrate and water, and the three temperatures are  $25^\circ\text{C}$ .,  $75^\circ\text{C}$ . and  $100^\circ\text{C}$ . The data are found in Tables 15, 16 and 17 (see reference to polytherms in Chapter I).

Suppose the original complex is at  $75^\circ\text{C}$ . and the composition

25% sodium nitrate,  
40% potassium nitrate.

This is marked *x* on the diagram and it is seen that at  $75^\circ\text{C}$ . it comes within the liquid field, thus giving a clear solution.

At  $25^\circ\text{C}$ . the complex, still at point *x*, comes within the potassium nitrate field. This means that on cooling from  $75^\circ\text{C}$ . to  $25^\circ\text{C}$ . potassium nitrate will crystallize out of the solution.

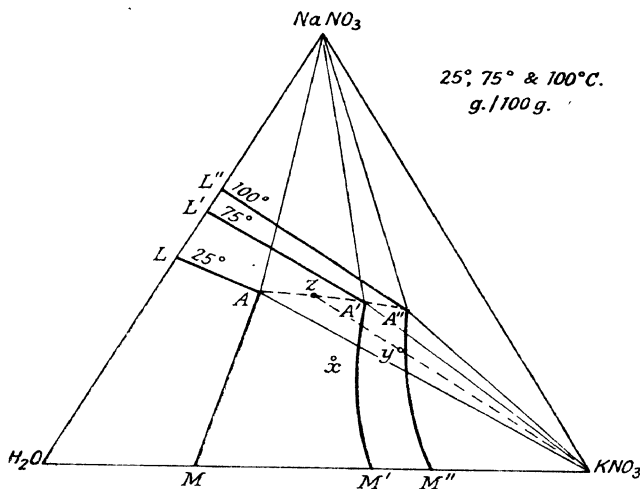
FIG. 16.— $\text{NaNO}_3$ . $\text{KNO}_3$  water.

TABLE 15

SODIUM NITRATE.POTASSIUM NITRATE.WATER  
(From E. Cornec and H. Krombach, *Caliche*, 1928)

Composition of saturated solutions at 25° C.

Ref. Letter.	$\text{NaNO}_3$ %	$\text{KNO}_3$ %	Solid Phase.
<i>L</i> . . . . .	47.9	0	$\text{NaNO}_3$
<i>A</i> . . . . .	40.3	19.1	$\text{NaNO}_3 + \text{KNO}_3$
<i>M</i> . . . . .	0	27.7	$\text{KNO}_3$

TABLE 16

SODIUM NITRATE.POTASSIUM NITRATE.WATER  
(From E. Cornec and H. Krombach, *Caliche*, 1928)

Composition of saturated solutions at 75° C.

Ref. Letter	$\text{NaNO}_3$ %	$\text{KNO}_3$ %	Solid Phase.
<i>L'</i> . . . . .	58.7	0	$\text{NaNO}_3$
	49.0	18.2	"
	42.4	30.9	"
<i>A'</i> . . . . .	38.3	39.1	$\text{NaNO}_3 + \text{KNO}_3$
	31.3	41.5	$\text{KNO}_3$
	18.7	47.7	"
<i>M'</i> . . . . .	0	60.4	"

TABLE 17  
SODIUM NITRATE. POTASSIUM NITRATE. WATER  
(From E. Cornec and H. Krombach, *Caliche*, 1928)  
Composition of saturated solutions at 100° C.

Ref. Letter	NaNO <sub>3</sub> %	KNO <sub>3</sub> %	Solid Phase.
<i>L</i> " . . . . .	63.7	0	NaNO <sub>3</sub>
	49.5	25.3	"
	41.1	40.0	"
<i>A</i> " . . . . .	36.7	48.1	NaNO <sub>3</sub> + KNO <sub>3</sub>
	29.7	51.4	KNO <sub>3</sub>
	18.7	57.7	"
<i>M</i> " . . . . .	0	70.9	"

The important point to note in this type of problem is that the composition of the complex does not alter. The part of the 75° C. diagram which especially concerns us is the curve *M'A'*. As the temperature is lowered towards 25° C. the complex remains at *x*, but the curve *M'A'* gradually moves across the chart until it reaches *MA* at 25° C. At an intermediate temperature the curve reaches *x* and it is at this stage that potassium nitrate begins to crystallize, giving potassium nitrate in the solid state and leaving a solution the composition of which must be on the line from the potassium nitrate corner through *x*. Thus at 25° C. the solution is where this line cuts the curve *MA*. At temperatures above 25° C. the solution will be somewhere between the above point and *x*.

Using the same diagram, Fig. 16, the point *y* represents a complex which, unlike *x*, is in the field of mixed solid at the low temperature. Suppose the problem is to obtain pure potassium nitrate. The composition of the complex at *y* is

27.0% sodium nitrate,  
51.5% potassium nitrate.

The complex will be in a different state at each of the three temperatures.

At 100° C. it will be completely liquid.

At 75° C. it will give potassium nitrate in the solid state and a solution on the curve *M'A'*.

At 25° C. it will give a mixture of potassium nitrate and sodium nitrate in the solid state and a solution of composition *A*.

In this case we are not only concerned with the curves *MA*, *M'A'*, and *M"A"*, but also with the lines from the potassium nitrate corner to *A*, *A'*, and *A"*. As the solution *y* is cooled from 100° C. the curve *M"A"* moves towards *M'A'*, and when this passes *y* then potassium nitrate begins to crystallize out of the solution. This is the desired result, but on further cooling the line from the potassium nitrate corner to *A'* (i.e. the *A'* line) moves towards the *A* line. After the *A'* line has passed the point *y* both potassium nitrate and sodium nitrate are thrown out of solution. Thus the mixture must not be cooled below the temperature at which the *A'* line reaches *y*. This temperature may be determined approximately as follows.

The curve joining *A*, *A'* and *A"* shows the movement of the point *A* with change of temperature. A straight line is drawn from potassium nitrate to *y* and produced to meet the curve *A'A"* at *z*. Call this the *z* line. Then the temperature at which the *A'* line coincides with the *z* line gives the lowest temperature to which the complex *y* may be cooled



to obtain pure potassium nitrate in the solid state. This temperature will also give the highest yield of pure potassium nitrate possible by cooling and the composition of the solution will be  $z$ . By interpolation the temperature is judged to be approximately  $50^{\circ}\text{C}$ .

To determine this temperature accurately further phase diagrams are necessary, that is curves at intermediate temperatures.

To summarize, the main principles in the practical application of a phase diagram are :

(1) When any substance (water, salt, or solution) is *added* to a complex the composition of the complex moves in a straight line *towards* the point representing that substance. Conversely, when any substance is *removed* the composition of the complex moves in a straight line *away* from the point representing that substance.

(2) When a complex is heated or cooled the position of the complex on the diagram remains unaltered, but the configuration of the diagram itself changes.

In either (1) or (2) the state of the complex may be predicted by the rules described in Chapter V.

In practice it is usual to have a number of operations either simultaneous or sequential. Thus a complex may be diluted and cooled at the same time ; it may be heated, evaporated and then cooled.

It might be pointed out at this stage, that as the diagrams are isotherms, it is necessary to know if any important change has taken place during the temperature range between the isotherms under consideration. Fig. 14 will serve as an example : the short curve  $BC$  is the saturation curve of  $\text{Na}_2\text{SO}_4$  at  $25^{\circ}\text{C}$ . At higher temperatures this curve is longer, while the saturation curve of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  becomes shorter and finally disappears at a specific high temperature. At lower temperatures the curve  $BC$  disappears and a solution is obtained which is saturated as to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and darapskite.

At an intermediate temperature, actually  $24.3^{\circ}\text{C}$ ., the curve  $BC$  becomes a point representing a solution saturated as to three solid phases,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$  and darapskite. Such a point is a system invariant point and it has no degree of freedom, the composition of the solution is fixed by nature and the temperature of the isotherm is also fixed. On the diagram which would be an isotherm at  $24.3^{\circ}\text{C}$ ., two curves would radiate from this invariant point at the break, but there would be three straight lines radiating to darapskite,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

In a similar way the curve  $AB$  will become a point at  $74^{\circ}\text{C}$ ., and there will be a solution saturated as to three solid phases,  $\text{NaNO}_3$ , darapskite and  $\text{Na}_2\text{SO}_4$ .

Finally, when studying isotherms evaporation is always considered as taking place without change of temperature. In practice evaporation is carried out at the boiling-point of the solution for the pressure conditions existing. Suppose the isotherm is at  $25^{\circ}\text{C}$ . and the amount of water to be removed has been calculated. Then, in the majority of cases, the solution may be heated to its boiling-point, the amount of water evaporated, the solution cooled back to  $25^{\circ}\text{C}$ . and agitated for sufficient time to obtain equilibrium with the same final result as if the evaporation had actually taken place at  $25^{\circ}\text{C}$ .

It might be well at this stage to consider more closely one of the *system invariant points* mentioned above : for example, the point representing a solution saturated as to  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$  and darapskite at  $74^{\circ}\text{C}$ . and when  $B$  and  $C$  coincide at a point.

Suppose this solution to be contained in a vessel with a fair quantity of the three solid phases added ; the temperature is  $74^{\circ}\text{C}$ . and equilibrium has been established. If the temperature is raised the darapskite phase will disappear, and if the temperature is lowered the points  $A$  and  $B$  will separate and form a curve.

To raise the temperature, heat must be given to the system, that is, heat is applied to the outer walls of the vessel but equilibrium must be maintained, because the phase rule only applies to systems at equilibrium. This means that in the experiment being considered, the heat must be applied sufficiently slowly and agitation of the mixture must be sufficiently vigorous, for the equilibrium not to be destroyed. Under these conditions the temperature does not rise. Darapskite is decomposed, but the composition of the solution remains unchanged until the darapskite phase has completely disappeared.

The phase rule indicates that the composition of the solution cannot change nor can the temperature alter while all three solid phases are present, *unless the equilibrium is destroyed*.

The principle of Le Chatelier states that, if heat is applied to a system, the phase reactions are such that heat will be absorbed. The decomposition of darapskite or, in other words, darapskite passing into solution and  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  being deposited, is an endothermic reaction, so by applying the principle of Le Chatelier it is possible to predict the direction of phase reactions when the necessary thermal data are available. When the solubility of a salt increases with rise of temperature the action of solution is endothermic and the action of crystallization is exothermic. Darapskite belongs to this class of salt because crystals of darapskite can be prepared by cooling a suitable solution. When the solubility of a salt is retrograde the action of solution is exothermic and crystallization is endothermic. Thus, when Glauber's salt or sodium nitrate dissolves in water, heat is absorbed, but when sodium sulphate dissolves heat is given out.

To return to the invariant solution in the vessel, when the darapskite phase has disappeared a degree of freedom has been gained. If heat is applied to the system the phase reactions will still be such as to cause the absorption of heat, but a temperature may now be selected and so the temperature will rise without the equilibrium being destroyed. When heat is applied to the vessel the temperature will rise and the composition of the solution, saturated as to sodium nitrate and sodium sulphate, will be fixed by the temperature. As the temperature rises heat will be absorbed because sodium nitrate will dissolve and sodium sulphate will be deposited, and both these reactions are endothermic.

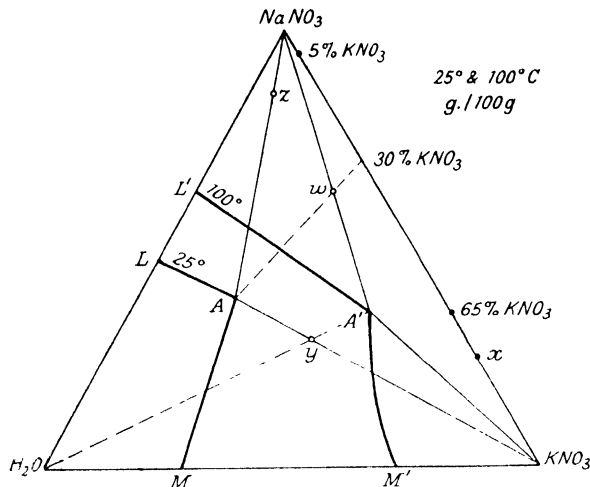
The temperature could have been made to rise before all the darapskite had been decomposed, that is, by applying a sufficient quantity of heat over a short period of time, but in that case the equilibrium would be destroyed. In practice the equilibrium is usually destroyed deliberately so that the reaction may be more rapid. In the example being considered sufficient heat would be supplied to overcome the resistance of the system and the darapskite would be decomposed rapidly. The system could then be allowed to regain equilibrium if necessary and at the temperature required.

It will thus be realized that, during the isothermal removal of water, according to the solid phases being deposited or dissolved, it will be necessary to supply heat or to remove heat in order that isothermal conditions may be maintained.

**A Series of Operations.** The following examples are typical of the application of three-component diagrams to industrial processes where several operations are combined. For convenience the same salts are used as for Fig. 16, but a new diagram is given, Fig. 17.

Three problems or examples will be considered, each being the separation of potassium and sodium nitrates. In the first case the original mixture is rich in potassium nitrate; in the second case it is less rich; and in the last case it only contains a small amount of the potassium salt.

(I) Suppose the first mixture contains 75% potassium nitrate and 25% sodium nitrate.

FIG. 17.— $\text{NaNO}_3$ .  $\text{KNO}_3$ . water.

This is marked  $x$  on the diagram. When water is added the complex moves in a straight line towards water and sufficient water must be added to bring the complex within the potassium nitrate field for the temperature to which the mixture is going to be cooled. In this example the temperature is assumed to be  $25^\circ\text{C}$ .

The water could be added to give a mixture at  $25^\circ\text{C}$ ., and such a mixture, if given sufficient time and agitation, would result in solid potassium nitrate, the sodium nitrate all being in solution. Such a method does not allow for the removal of insoluble impurities such as earthy matter. It is more usual to work at a higher temperature, say  $100^\circ\text{C}$ ., and, after filtration or settling, to obtain the crystals by cooling the clear liquid.

Water must, therefore, be added not only to bring the complex within the *potassium nitrate field for  $25^\circ\text{C}$* ., but also to bring it within the *liquid field for  $100^\circ\text{C}$* . In the example taken (point  $x$ ) water must be added until the complex reaches the curve  $M'A'$ . This will give a solution at  $100^\circ\text{C}$ . which can be filtered or settled. The clear liquid on cooling to  $25^\circ\text{C}$ . will then deposit pure potassium nitrate.

If the original mixture of salts contains slightly less potassium nitrate, say 65%, then the complex must be moved beyond the curve  $M'A'$  in order to enter the potassium nitrate field for  $25^\circ\text{C}$ . The final solution would then be unsaturated at  $100^\circ\text{C}$ ., and a smaller yield of potassium nitrate will be obtained on cooling.

(II) With an original mixture containing 30% potassium nitrate and 70% sodium nitrate a different kind of problem arises because the addition of water cannot give a complex within the potassium nitrate field for  $25^\circ\text{C}$ . (nor for any temperature above  $25^\circ\text{C}$ .). This problem is approached from the opposite direction, that is, solid sodium nitrate is removed in order to obtain a solution enriched in the potassium salt.

Water is added to the original mixture in sufficient quantity to move the complex into the sodium nitrate field for  $100^\circ\text{C}$ . The complex need only be moved along the line towards water as far as the boundary of the sodium nitrate field for  $100^\circ\text{C}$ .; this is not

point  $w$  but slightly above. At this boundary all the potassium salt will be in solution, the solid phase being sodium nitrate. The composition of the solution is given at point  $A'$  on the diagram. Thus, after the separation of the solid sodium nitrate, a solution is obtained which contains both sodium and potassium nitrate, but which has been enriched in the potassium by the removal of some of the sodium, the temperature having been maintained at  $100^{\circ}\text{C}$ .

Even now the enriched solution will not give potassium nitrate on cooling, the point  $A'$  being within the mixed field for  $25^{\circ}\text{C}$ . The addition of water to the solution will move its position into the potassium nitrate field for  $25^{\circ}\text{C}$ . Water is therefore added, sufficient to bring the solution just within that field, that is to the point  $y$ . It is not essential during this last addition of water to keep the temperature at  $100^{\circ}\text{C}$ . The solution represented by the point  $y$  is cooled to  $25^{\circ}\text{C}$  and potassium nitrate is obtained as crystals. The mother liquor has the composition represented by the point  $A$ .

The mother liquor can be used to dissolve a further quantity of raw material. Thus, if solution of composition  $A$  is added to the 30% potassium nitrate mixture, a complex may be obtained of a composition which lies on the boundary of the sodium nitrate field for  $100^{\circ}\text{C}$ . This complex is at  $w$  and lies on the straight line between  $A$  and 30% potassium nitrate. If this complex is heated to  $100^{\circ}\text{C}$ , all the potassium nitrate will dissolve and solid sodium nitrate can be removed. The solution will have the composition  $A'$  and the rest of the process may be carried out exactly as described above, the final result being the production of crystals of potassium nitrate and a mother liquor of composition  $A$ . Thus a cyclic process has been developed.

(III) If the raw material is very weak in potassium nitrate, say 5%, the first operation of the above cycle would give a mixture containing such a low percentage of liquid that it would be impracticable to work at  $100^{\circ}\text{C}$ , and the separation of the solid from the liquid at  $100^{\circ}\text{C}$  would present innumerable difficulties. This introduces the third example.

The mixture containing 5% potassium nitrate and 95% sodium nitrate can be conveniently treated with cold water and, although the quantity will be small, it can be allowed to drain through the mass and recirculated until a saturated solution is obtained. Sufficient water must be circulated so that the composition of the mixture is represented by the point  $z$  on the diagram, this being on the boundary of the sodium nitrate field for  $25^{\circ}\text{C}$ .

The saturated solution will have the composition  $A$ , the solid left behind being sodium nitrate. To obtain potassium nitrate crystals the saturated solution  $A$  is concentrated by the evaporation of water, thus moving the complex in a straight line through  $A$  away from the water corner. The evaporation is continued until the complex reaches the boundary of the sodium nitrate field for  $100^{\circ}\text{C}$ . At this point the solution has the composition  $A'$ , and the solid which has been deposited is sodium nitrate. The solution  $A'$  is separated from the sodium nitrate at  $100^{\circ}\text{C}$ , and is diluted with water and cooled as in the previous example. This will give potassium nitrate crystals and mother liquor of composition  $A$ .

The mother liquor  $A$  is already saturated with potassium nitrate at  $25^{\circ}\text{C}$ , and therefore fresh water must be used for treating a further batch of raw material. The mother liquor  $A$  is concentrated by evaporation together with the next batch of cold circulating liquor which has the same composition  $A$ . As in the previous example, the process is a complete cycle of operations which may be repeated indefinitely. In practice, of course, small impurities will accumulate and some mother liquor may have to be rejected or purified.

**Isothermal Invariant Point in Field of Pure Salt at Lower Temperature.** In the above examples of a series of operations, the phase diagram taken was one where the

solubility of both salts at the invariant point increases with increasing temperature. Thus, in Fig. 17 at  $A'$ , the solution contains more potassium nitrate and more sodium nitrate than at  $A$ . In other words, the triangle  $\text{NaNO}_3 \cdot A' \cdot \text{KNO}_3$ , the mixed solid field at  $100^\circ \text{C}$ ., lies entirely within the triangle  $\text{NaNO}_3 \cdot A \cdot \text{KNO}_3$ , the mixed solid field at  $25^\circ \text{C}$ . The point  $A'$ , representing the hot solution saturated as to both salts, is within this mixed field for the lower temperature. A curve drawn between  $A$  and  $A'$  is the path of the isothermal invariant points as the temperature changes from  $100^\circ$  to  $25^\circ \text{C}$ ., and if this curve is produced it will cut the side of the triangle between the two salts.

When a solution represented by  $A'$  is cooled both salts are deposited and the solution remains saturated as to both salts. The solution must be diluted if one of the salts is to be obtained pure in the solid phase on cooling. Many pairs of salts behave in this way.

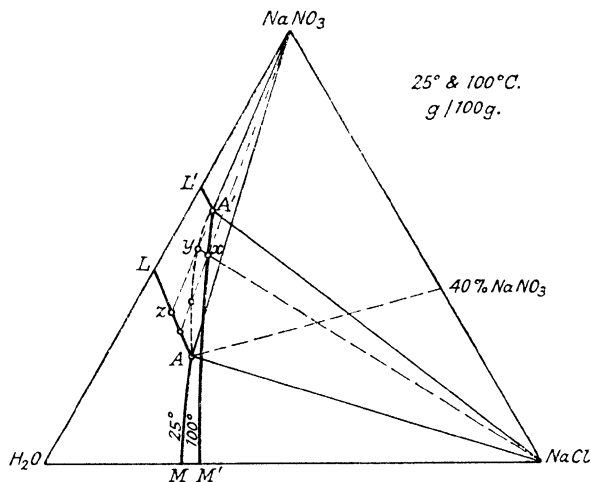


FIG. 18. — $\text{NaNO}_3$ . $\text{NaCl}$  water.

Part of this diagram has been distorted for clarity.

It is quite common, however, for a pair of salts to behave differently, one of the salts at the invariant point increasing in solubility at the expense of the other. When such a solution, saturated as to both salts, is cooled, the more soluble salt crystallizes out and the solution becomes unsaturated with the less soluble salt. The system sodium nitrate, sodium chloride and water is a good example of this case. Tables 18 and 19 give the data, and Fig. 18 is the diagram; the temperatures chosen are  $25^\circ \text{C}$ . and  $100^\circ \text{C}$ .

It will be noticed that the curve  $A'A$  if produced would not cut the side of the triangle  $\text{NaNO}_3 \cdot \text{NaCl}$  and that the triangle  $\text{NaNO}_3 \cdot A' \cdot \text{NaCl}$  does not lie entirely within the triangle  $\text{NaNO}_3 \cdot A \cdot \text{NaCl}$ .

An example will now be taken using the diagram to work out a method of separating sodium nitrate from a raw material containing sodium chloride. Suppose the raw material contains 40% sodium nitrate and 60% sodium chloride.

If the correct amount of water is added to the raw material and the temperature maintained at  $100^\circ \text{C}$ ., a complex may be obtained on the boundary of the sodium chloride

## AQUEOUS SOLUTION AND THE PHASE DIAGRAM

TABLE 18

SODIUM NITRATE.SODIUM CHLORIDE.WATER  
(From E. Cornec and A. Chretien, *Caliche*, 1924)  
Composition of saturated solutions at 25° C.

Ref. Letter	NaNO <sub>3</sub> , %	NaCl, %	Solid Phase.
<i>L</i> . . . . .	47.8	0	NaNO <sub>3</sub>
	43.7	3.2	"
	40.5	6.2	"
	36.0	9.6	"
<i>A</i> . . . . .	32.0	13.3	NaNO <sub>3</sub> + NaCl
	25.5	15.9	NaCl
	18.4	18.9	"
	9.7	22.6	"
<i>M</i> . . . . .	0	26.6	"

TABLE 19

SODIUM NITRATE.SODIUM CHLORIDE.WATER  
(From E. Cornec and A. Chretien, *Caliche*, 1924)  
Composition of saturated solutions at 100° C.

Ref. Letter	NaNO <sub>3</sub> , %	NaCl, %	Solid Phase.
<i>L'</i> . . . . .	63.7	0	NaNO <sub>3</sub>
	60.6	2.8	"
<i>A'</i> . . . . .	59.4	4.0	"
	57.5	5.6	NaNO <sub>3</sub> + NaCl
	56.9	5.8	NaCl
	55.7	6.2	"
	54.2	6.6	"
	50.7	7.7	"
	48.7	8.2	"
	43.0	10.2	"
<i>M'</i> . . . . .	33.9	13.4	"
	24.0	17.6	"
	0	28.6	"

field for 100° C. Solid sodium chloride may be separated from the solution, which solution will have a composition *A'*. This solution is already within the sodium nitrate field for 25° C. and on cooling will deposit the nitrate. This differs from the previous example of Fig. 17 in that no dilution of solution *A'* is necessary. An inspection of the diagram, Fig. 18, shows that the mother liquor obtained at 25° C. will be a point on the curve *LA* where the line from sodium nitrate through *A'* meets the curve. This is not at *z* but slightly nearer to *L*.

In order to have a cyclic process the mother liquor must be used with fresh raw material. Sufficient raw material is taken to give a complex on the boundary of the sodium chloride field for 100° C., that is a similar position to that obtained when using water except that the complex is closer to *A'*. The complex at 100° C. will give solution *A'* and solid sodium chloride. The sodium chloride is removed and the solution *A'* is cooled to 25° C. to produce sodium nitrate crystals and the same mother liquor as before.

If the raw material contains more or less nitrate than 40% the same procedure will result in the same solution,  $A'$ , and a similar cyclic process.

For convenience of description when following an operation on the diagram a complex has been taken to be on the boundary of a field. In actual practice the complex would generally be moved to a point just within the desired field. This avoids the danger of contamination. Also on the large scale the time to reach equilibrium is often too long to be economical. Thus when making mixtures the quantities are adjusted accordingly.

In the present example where the 40% raw material is treated with mother liquor the operation of dissolving need not be continued long enough to give the solution  $A'$ , but to give a solution on the curve  $M'A'$  at say  $x$ . When this solution is cooled a rather interesting phenomenon occurs.

The solution is saturated with chloride but not with nitrate, and the first result of cooling will be the crystallization of sodium chloride. The composition of the solution will therefore move in a line through  $x$  away from sodium chloride. When the composition of the solution reaches the curve  $A'A$  at  $y$  the solution is saturated with both salts. This is at a temperature between  $100^{\circ}\text{C.}$  and  $25^{\circ}\text{C.}$  since the curve  $A'A$  is not an isotherm, but the path of the invariant point at temperatures from  $100^{\circ}\text{C.}$  to  $25^{\circ}\text{C.}$  If solution  $y$  is separated from the deposited sodium chloride and the solution cooled to  $25^{\circ}\text{C.}$  sodium nitrate will be deposited and a mother liquor will be obtained on the curve  $LA$  represented by the point  $z$ , which is on the line from sodium nitrate through  $y$ .

If, on the other hand, the deposited sodium chloride is not removed and the complex  $x$  cooled sodium nitrate will be deposited and sodium chloride will be redissolved. This redissolving will proceed so that from the point  $y$  the composition of the solution follows the curve  $A'A$ . When all the sodium chloride has dissolved the solution will be where the line from sodium nitrate through  $x$  meets the curve  $A'A$ . Further cooling to  $25^{\circ}\text{C.}$  will give a final solution where the same line meets the curve  $LA$ . Thus in order to determine the *final* result of cooling the intermediate deposition of sodium chloride could have been ignored, but it is necessary to know the actual path of crystallization because, in this case, it has shown the necessity of agitation during cooling.

It may also be noted that the yield of nitrate is greater by leaving the chloride to redissolve than if it were removed before cooling.

**A Quantitative Example of a Cyclic Process.** A cyclic process can be outlined on a phase diagram in the manner already described, but it is also necessary to know the quantities involved in each operation. On p. 56 a cycle was outlined, using Fig. 17, for the production of potassium nitrate from a raw material containing sodium nitrate. The calculations below show how the cycle can be worked out quantitatively. It will be realized that a larger diagram than Fig. 17 was used for this purpose

Briefly, the cycle moved on the diagram round the quadrilateral  $wa'A'yA$ . The complex  $w$  was first prepared and from this the solution  $A'$  was obtained. The latter solution was diluted to  $y$  and on cooling gave solution  $A$ , which was used for the preparation of a further quantity of complex  $w$ .

The data required are :

(a) The composition of the raw material (as given in the example on p. 55) :

70.0% sodium nitrate  
30.0% potassium nitrate.

(b) The composition of  $A'$  (obtained from table) :

36.7% sodium nitrate  
48.1% potassium nitrate  
25.2% water.

(c) The composition of  $A$  (obtained from table) :

40.3% sodium nitrate  
19.1% potassium nitrate  
40.6% water.

(d) The ratio of solution  $A$  to the raw material for complex  $w$ . (Obtained from diagram by the method described on p. 33.)

8.7 units solution  $A$   
31.9 units raw material

---

40.6 units complex  $w$ .

(e) The ratio of solution  $A'$  to solid sodium nitrate (obtained from diagram) :

36.4 units solution  $A'$   
26.9 units solid sodium nitrate

---

63.3 units complex  $w$ .

(f) The proportion of water to be added to  $A'$  to give solution  $y$  (obtained from diagram) :

69.8 units solution  $A'$   
15.0 units water

---

84.8 units solution  $y$ .

(g) The ratio of solution  $A$  to solid potassium nitrate for complex  $y$  (obtained from diagram) :

60.3 units solution  $A$   
20.6 units solid potassium nitrate

---

80.9 units solution  $y$ .

The cycle begins with mother liquor from a previous cycle, in this case solution  $A$ . Suppose that 100 parts of raw material are to be treated. From the data (d) above :

31.9 parts <sup>1</sup> raw material require 8.7 parts solution  $A$   
100        "        "        "        "        27.3        "        "        "

giving 127.3 parts complex  $w$ .

At 100° C. the complex  $w$  yields solid sodium nitrate. From the data (e) :

63.3 parts complex  $w$  give 26.9 parts solid sodium nitrate  
127.3        "        "        "        "        54.1        "        "        "

leaving 73.2 parts solution  $A'$ .

<sup>1</sup> Parts are by weight throughout this calculation.



The water required to produce solution  $y$  is obtained from the data ( $f$ ):

69.8	parts	solution $A'$	require	15.0	parts	water
73.2	"	"	"	15.7	"	"

giving 88.9 parts solution  $y$ .

At 25° C. the complex  $y$  yields solid potassium nitrate. From the data ( $g$ ):

80.9	parts	complex $y$	give	20.6	parts	solid potassium nitrate
88.9	"	"	"	22.6	"	"

leaving 66.3 parts mother liquor (solution  $A$ ).

Summarizing:

The raw material	.	.	.	.	.	100.0	parts
is mixed at 100° C. with mother liquor $A$	.	.	.	.	.	27.3	"
From this is removed solid sodium nitrate	.	.	.	.	.	54.1	"
leaving solution $A'$	.	.	.	.	.	73.2	"
to which is added water	.	.	.	.	.	15.7	"
The diluted solution is cooled to 25° C. and gives solid							
potassium nitrate	.	.	.	.	.	22.6	"
and mother liquor $A$	.	.	.	.	.	66.3	"

The cycle begins with 27.3 parts mother liquor  $A$  and finishes with 66.3 parts, an increase of 39 parts. This is due to the 15.7 parts of water which has been introduced and which must be removed by evaporation. Thus 27.3 parts of the final mother liquor are returned to the dissolving vessel in order to treat a second charge of raw material, leaving 39 parts to go to an evaporator.

It is obvious that 15.7 parts of water can only be removed from the 39 parts of mother liquor by taking the solution to dryness. If, on the other hand, the 39 parts are concentrated until the solution has the composition  $A'$ , sodium nitrate being precipitated, less than 15.7 parts of water will be evaporated. On diluting and cooling a further quantity of mother liquor  $A$  will be obtained which will also require concentrating. This might be continued indefinitely leaving a smaller quantity of mother liquor each time.

In practice a stock of mother liquor would be carried and used to feed both dissolving vessel and evaporator. For the purpose of costing it must be noted that for the production of 22.6 parts of potassium nitrate 15.7 parts of water must be evaporated. In order to produce 30 parts of potassium nitrate which will eventually be obtained from the original 100 parts of raw material more water must be introduced and evaporated, as explained above.

In order that the concentrated liquor from the evaporator may be returned to the cycle at an appropriate stage the mother liquor would only be concentrated to the boundary of the sodium nitrate field for 100° C. On the diagram the evaporation line is drawn as from the water corner through  $A$  and produced to meet the above boundary at which point evaporation is discontinued. In this case the point happens to be very near to  $w$  and so it is not marked on the diagram, but we will call it  $w'$ .

The proportion of water to be evaporated from 100 parts of mother liquor is determined by taking the proportions of the line  $w'$  to  $A$  and  $H_2O$  to  $w'$ . These are 32 units and

91.5 units respectively, indicating that 32 parts of water must be removed from 91.5 parts of mother liquor. That is 35 parts of water from 100 parts of mother liquor. This, at  $100^{\circ}\text{C}.$ , will give solid sodium nitrate and solution  $A'$ , the latter being added to the cycle at the  $A'$  stage.

## CHAPTER VII

### DETERMINATION OF SOLUBILITY FOR PHASE DIAGRAMS

This chapter follows the study of three-component systems and so the methods given here are applied to three-component diagrams. They may, however, be used for all systems by suitable adjustment.

The curves in three-component diagrams trace out the points of solutions *saturated with respect to one or more salts*. Thus, if any mixture of water and the two salts is taken which leaves some crystals undissolved, the analysis of the solution must give a point on one of the curves. By taking a range of mixtures a number of saturated solutions can be obtained and a sufficient number of points determined to draw all the curves in the diagram. To complete the diagram it is necessary to know with what salt or salts each solution is saturated, and so steps must be taken to determine the composition of the undissolved crystals. By filtering and analysing the crystals an approximate idea may be formed, but this is not sufficiently accurate as some mother liquor will be left in the filtered crystals. As it is practically impossible to remove all the mother liquor a method is used which allows for the presence of mother liquor and therefore no attempt is made to remove it. This method was introduced by F. A. H. Schreinemakers in 1893 and is known as the method of "wet residues" (*Z. physik. Chem.*, 1893 **11**, 81).

**Method of Wet Residues.** It will be remembered that if any complex is marked on the diagram it lies on the straight line joining its solution with its solid. If, therefore, some mother liquor remains with the solid the composition of the wet residue must also lie on the same straight line, but nearer to the solid. By analysing a solution and its wet residue two points can be plotted on a diagram and a straight line is drawn through them. The composition of the solution gives a point on the curve; the composition of the solid phase must lie somewhere on the straight line beyond the position of the wet residue.

If several solutions and their wet residues are analysed and their straight lines plotted, some lines will be found to cross at points representing solid compounds, while others cross at the point representing solution. In the latter case the solution thus indicated is an invariant one at a break in the curve, showing that the complexes lie in a mixed field.

A convenient way of carrying out this method is to take a range of mixtures of the two salts; for example, take 90% of one salt and 10% of the other for one mixture. Then take 80% of the one and 20% of the other, and so on to 10% and 90%. Water is added to each mixture, but *not* in sufficient quantity to dissolve all the salt. The whole is agitated for several hours at the desired temperature in order that equilibrium may be attained.

The mixture is allowed to settle while still maintained at the specified temperature, and some of the clear solution is analysed. This analysis gives the point on the curve.

The remainder of the solution is decanted and the wet residue of crystals and solution is analysed as a whole. The best way to do this is to weigh the wet residue, dissolve it in water, make up to volume and analyse the resulting solution. Such analysis is calculated as a percentage of the wet residue and gives the second point on the diagram.

For each original mixture two analyses are obtained, one representing solution, the other representing wet residue. The solution points are joined to form the curves. The points on the curves are joined by straight lines to their respective wet-residue points and

## AQUEOUS SOLUTION AND THE PHASE DIAGRAM

the lines produced. An inspection of the diagram will now show whether sufficient points have been determined, and any deficiency is made up by preparing more mixtures within the range required. Not less than two lines and preferably more should meet at each solid phase and at each invariant point.

TABLE 20

AMMONIUM CHLORIDE-AMMONIUM NITRATE-WATER, 25° C.  
(From Prutton, Brosheer and Maron, *J.A.C.S.*, 1935, **57**, 1657)

Saturated Solution		Wet Residue.		Solid Phase
$\text{NH}_4\text{NO}_3$ %	$\text{NH}_4\text{Cl}$ %	$\text{NH}_4\text{NO}_3$ %	$\text{NH}_4\text{Cl}$ %	
67.73	0	—	—	$\text{NH}_4\text{NO}_3$
66.27	2.00	88.20	0.79	"
64.73	3.82	88.00	1.34	"
62.24	5.58	90.25	1.65	"
61.68	6.97	87.65	2.28	"
60.37 <sup>1</sup>	9.36	62.0	29.0	$\text{NH}_4\text{NO}_3 + \text{NH}_4\text{Cl}$
		53.0	36.5	
		38.5	51.5	
53.49	11.08	23.31	62.22	"
44.50	13.60	17.99	66.03	$\text{NH}_4\text{Cl}$
36.99	15.80	13.63	66.29	"
29.57	18.20	12.49	68.74	"
19.05	21.81	7.09	72.75	"
9.14	25.21	4.12	71.60	"
0	28.33	—	—	"

<sup>1</sup> Mean of three determinations.

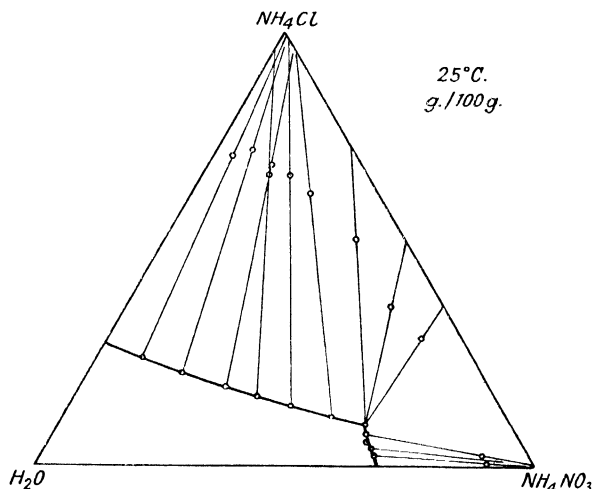


FIG. 19.— $\text{NH}_4\text{Cl}$ - $\text{NH}_4\text{NO}_3$ -water. Wet-Residue Method of Plotting.

The following example illustrates the method for a pair of simple salts. Table 20 gives figures obtained by Prutton, Brosheer and Maron for ammonium nitrate and ammonium chloride at 25° C. (*J.A.C.S.*, 1935, 57, 1657). Fig. 19 is the diagram. This shows the importance of a number of determinations as the lines only approximately cross within the ammonium chloride field, but there is no break in the ammonium chloride curve and the general trend of the lines is to meet at the ammonium chloride corner. This is the usual experience, and it is necessary to take a general view of the diagram as a whole.

It is not proposed to give any further examples, but if a double compound exists, or a hydrate, the lines will indicate its presence by their obvious convergence on a point which inspection will show to be a definite compound.

Technical literature provides numerous examples of recent work, and the following might be taken as studies of more complicated investigations for the determination of equilibria for phase diagrams.

Magnesium sulphate, cadmium sulphate and water at 25° and 40°. W. C. Vosburgh *et al.*, *J.A.C.S.*, 1940, 1472.

Manganous nitrate—nitric acid—water at 20° C. W. W. Ewing and C. F. Glich, *J.A.C.S.*, 1940, 2174.

An omnibus paper on:  $\text{CaCl}_2\text{—Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$  25°,  $\text{CaCl}_2\text{—Ca}(\text{ClO}_3)_2\text{—H}_2\text{O}$  25°,  $\text{SrCl}_2\text{—Sr}(\text{NO}_3)_2\text{—H}_2\text{O}$  25°,  $\text{KNO}_3\text{—Pb}(\text{NO}_3)_2\text{—H}_2\text{O}$  0°, by William F. Ehret, *J.A.C.S.*, 1932, 3126.

Sodium carbonate—calcium carbonate—water (at several temperatures). C. R. Bury and R. Redd, *J.C.S.*, 1933, 1161. The data are given in this paper, but the isotherms have not been plotted. A cross-section is given of the prism with temperature as the ordinate. This could be obtained by mounting the isotherms to form a triangular prism.

Calcium sulphate, ammonium sulphate and water at several temperatures. A. E. Hill and N. S. Yanick, *J.A.C.S.*, 1935, 645. This is an example where one component has a very low solubility.

**The Synthetic Complex Method.** A method which has been found to give results quite accurate enough for ordinary works' use is a modification of the above. Instead of analysing the wet residue a complex is prepared of known composition and the solution only is analysed. This, again, gives two points on the diagram: the solution point on the curve and the complex point which replaces the wet residue point. Hill and Ricci, *J.A.C.S.*, 1931, 53, 4305, say that the complex method is as accurate or more accurate than the residue method if algebraic extrapolation of the tie lines is used.

A range of salt mixtures is prepared and water is added to each mixture as before, but in this case the amount of water used must be known. It is convenient to run the water from a burette into a stoppered bottle containing the salt mixture. The composition of each complex is known and its composition can be calculated to percentages and marked on the diagram.

The bottles are agitated at the desired temperature for several hours until equilibrium is reached. Care is required to avoid loss of water by evaporation, because it is assumed that the composition of the complex remains as calculated from the quantities taken. For the same reason the salts used must be as pure as possible.

A sample of the solution resulting from each complex is taken and analysed exactly as in the method of wet residues. These solution points are plotted on a diagram to form the curves, and by joining them to their respective complex points the solid phases are indicated. The distance on the diagram from a solution point to a complex point is less

than from a solution point to a wet residue. This increases the error when the line is produced beyond the complex point, but for the majority of simple cases there is sufficient accuracy. By algebraic extrapolation the complex point may be plotted without any water content and thus the error can be reduced (see p. 67).

This method is quite suitable when working at low temperatures, say not above 40° C. It is obvious that at 100° C. it is difficult to avoid some evaporation of the water content.

The reader must not be misled by the apparent simplicity of the preceding. When investigating a new system, in which very little is known about the existence or non-existence of intermediate compounds or hydrates, great care and patience are necessary to ensure that every solid phase is found. This is especially so where the compositions of different solid phases are very much alike and are therefore close together in the diagram.

It is sometimes necessary to obtain further confirmation of a particular solid phase by microscopic examination of the crystals.

**Apparatus.** Many methods are in use for obtaining equilibrium between solid and liquid and for removing sufficient solution for analysis. Whatever method and apparatus are chosen it is important that the salts and solution shall be in intimate contact at a constant temperature for a period long enough to bring about equilibrium. This time varies from a few minutes to several weeks, but for most cases the time taken is a few hours.

When equilibrium has been reached a sample of the clear liquor must be removed and weighed under such conditions that there is no change in its composition. For instance, there must be no loss of crystals through cooling, nor must there be any loss of water by evaporation. The clear liquor is usually obtained by allowing the complex to settle, for several hours if necessary, the temperature being maintained constant.

A simple type of apparatus is a stoppered bottle fixed in a shaking device and submerged in a water-bath at a controlled temperature. The shaking device may be a wheel fixed in a vertical position, so that the bottles tied to the spokes are turned over from end to end within the water-bath.

An elaborate thermostat, with automatic temperature control, can be used as the water-bath, or a fairly large water container can be used with hand control when working near room temperature. A carbon filament lamp, with the glass immersed in the water, makes a very simple electric heater.

When the agitation period is complete the bottles are removed from the wheel and the contents are shaken down without removing the bottles from the water-bath. They are placed in a rack below the surface of the water and left to settle until the supernatant liquor is clear. The bottles are then raised so that their tops are just above water level. The stoppers are dried with filter paper and removed.

Choosing a small dry pipette with a quick delivery, a sample from each bottle is taken and delivered into a weighing bottle. If the pipette is warmed above the temperature of the liquid there should be no fear of crystallization and the evaporation can be ignored. A pipette is suggested as a convenient instrument, but no attempt need be made to measure the sample. The amount taken is *weighed*, made up to a definite volume and analysed.

If the synthetic complex method is being used the remainder of the contents of the bottles may be discarded. With the method of wet residues as much clear liquor as possible is removed with a larger pipette, and the bottle containing the wet residues is re-stoppered, removed from the water-bath, dried and weighed at room temperature. The contents are dissolved in water, made up to a definite volume and analysed.

In the method of wet residues the object of removing as much liquor as possible before

analysing is to obtain a wet residue point as far from the solution point as possible. In the synthetic complex method there is a limit to the distance obtainable between the two points, but in order to have them as far distant as possible the complex should contain the minimum amount of water, which will give a mixture that can be agitated and settled to give a clear sample of solution.

There are two possible errors, the analytical error and the geometrical error in producing a line joining two points very close together. The analytical error is unavoidably multiplied, but the geometrical error can be avoided by a simple calculation. Suppose the synthetic complex to be :

Salt A . . . .	20%
Salt B . . . .	30%
Water . . . .	50%

and the solution on analysis gives :

A . . . .	4%
B . . . .	16%
Water . . . .	80%

80 parts water contain  $4A + 16B$

50 „ „ „  $2.5A + 10B$ .

This amount of solution is subtracted from the complex giving

$$\left. \begin{array}{l} 20 - 2.5 = 17.5A \\ 30 - 10.0 = 20.0B \end{array} \right\} 37.5 \text{ total} \\ \text{and no water.}$$

Thus, if all the water could be removed from the complex as solution, the dry residue would be

$$\begin{array}{l} 53.3\% A \\ 46.7\% B \end{array}$$

This point, when marked on the edge of the diagram, gives the correct extrapolation of the complex point. It does not necessarily represent any existing solid phase, but the line joining this point to the solution point must pass through the true solid phase.

Instead of obtaining equilibrium mixtures in stoppered bottles the work can be carried out in open beakers using glass agitators driven by a small motor. This is obviously only suitable for room temperatures or lower where evaporation loss is very small.

More elaborate apparatus has been designed suitable for all temperatures and for more accurate work. An apparatus for temperatures almost to the boiling-point of the solution is illustrated in Fig. 20 A. This was used by Prof. Cornec and his collaborators at the University of Strasbourg and is described in *Caliche*, 1924.

The apparatus comprises a strong glass tube, *a*, provided with a rubber stopper which has three holes. A short length of glass tube is fitted into each hole with about one inch protruding so that the vessel can be submerged in the water-bath.

The central hole takes a glass rod agitator *b* which is rotated at 200 to 500 r.p.m. by means of a small motor and pulley. It is advantageous to have the pulley and its spindle suitably supported and to connect the spindle to the glass rod of the agitator by means of a short length of rubber tubing. This facilitates the disconnection of the apparatus.

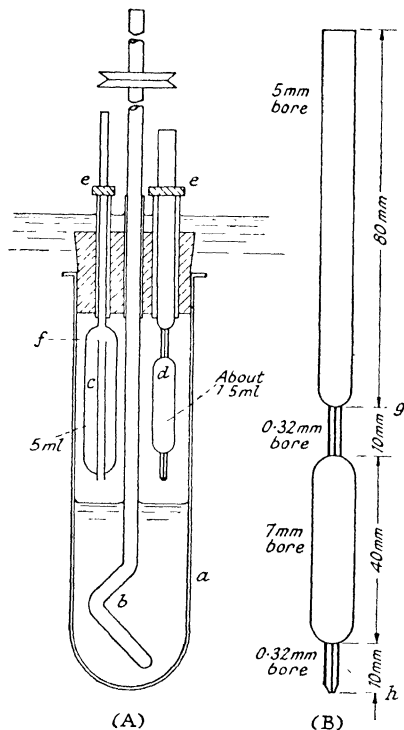


FIG. 20.

The two outer holes are to take pipettes for sampling, and either or both of these pipettes are used according to the nature of the solution. The pipette *c* of about 5 ml. capacity is for taking the sample of clear solution when equilibrium has been established. During the agitation period the pipette is supported out of the liquor by means of a rubber band *e* which also seals the opening. The sample is taken by removing the rubber band, lowering the pipette and aspirating the solution to just above the level *f*. The pipette is raised again, the rubber band replaced and the pipette allowed to drain.

If the wet residue is required, the remainder of the clear liquor is removed by inserting an ordinary pipette into the other pipette opening. The apparatus is taken from the water-bath and the rubber stopper is removed in order to withdraw the pipette. The pipette and the vessel are dried and weighed separately at room temperature for subsequent analysis. The wet residue adhering to the agitator can be ignored.

In carrying out the method as described above there is no means of knowing when equilibrium has been reached. The smaller pipette *d* is introduced to overcome this difficulty when necessary. One means of knowing that equilibrium has been reached is to establish that the specific gravity of the solution is constant. The pipette *d* provides a means of determining the relative density from time to time.



The pipette is illustrated on Fig. 20 B. The two short lengths of capillary tube have a bore of approximately 0.3 mm. A capillary tube of this bore will support a column of water about 10 cm. and slightly more of salt solutions. Therefore, if the length from *g* to *h* is made less than 10 cm., say 7 or 8 cm., then, when the pipette is filled above *g* and allowed to drain, the level of the liquor will fall to *g* and remain there. This means that the pipette will automatically retain the same *volume* of liquor whatever its composition.

The pipette is inserted into the apparatus during the agitation, and is therefore at the same temperature as the solution. In order to take a sample the agitation is stopped, the liquor is allowed to settle and the pipette lowered into the solution and filled. The pipette is raised clear of the liquor, allowed to drain and removed with its charge of solution. It is wiped clean with filter paper, left to cool on its side and weighed. A further sample can be taken, say one hour later, and if there is no change in weight, it may be assumed that equilibrium has been attained.

The reason for cooling and weighing the charged pipette on its side is that as soon as it begins to cool the solution contracts and empties the capillaries. In this condition the pipette would discharge its contents if kept vertical.

If the pipette is calibrated for the temperature of the experiment the weighings will give the actual specific gravity, a figure which may be very useful. The accuracy of this type of pipette is of a high order. A pipette which held 1.7858 g. of water at 20° C. was found to give a variation over a series of ten weighings of only 0.0002 g.

When the solution is rich in salts the contents of the small pipette *d* are sufficient for analysis and pipette *c* is not required. When only one pipette is being used, whether *c* or *d*, the other opening must be stoppered.

**Thermal Analysis.** A simple method for the determination of transition points for phase diagrams takes advantage of the fact that changes of phase are associated with absorption or liberation of heat. If a cooling curve is plotted for a complex the curve follows the regular form for a body radiating heat, and there are no irregularities in the curve as long as there are no phase or chemical reactions during the cooling. If a phase reaction takes place, then heat will be generated and the rate of cooling will be affected. This will be seen on the curve by a change in slope. The curve is usually plotted with temperature as ordinate and time as abscissa, and the slope of the curve, when a phase reaction is taking place, is to approach more nearly to the horizontal, i.e. the rate of cooling is retarded.

The critical temperatures are those where a particular phase reaction commences or ceases, and they are therefore indicated by the junctions of the different slopes on the cooling curve. These temperatures mark the boundaries of different fields of polythermal phase diagrams.

The phase reaction on cooling, or, more accurately, on removing heat from the system, is always exothermic. This is according to the Principle of Le Chatelier whereby the reaction is such as to resist the attempted change. The liberation of heat in this case is an attempt to maintain the temperature in spite of the removal of heat. Conversely, on heating a system the phase reaction will always be endothermic. Thus, in every case, whether heating or cooling, the curve will be altered to be more nearly horizontal at the point of change from a system with no phase reaction to one with a phase reaction.

When a system is invariant (condensed) then it is not possible to choose temperature as a degree of freedom. Thus, if heat is removed from a system and it reaches a temperature at which the phase reaction makes the system invariant, then the temperature will remain

constant until the phase reaction is complete. In this case the cooling curve becomes horizontal. The typical case of this is where a pure substance of one component, or a pure compound, is cooled and changes from liquid to solid. The temperature is the melting-point of the substance. As soon as the smallest trace of solid appears in the liquid the extra phase renders the system invariant and, until the liquid has all disappeared (by solidification), the temperature cannot again alter. The heat liberated is the latent heat of the molten substance, and the temperature will remain constant at the melting- (or solidification-) point until there is no more liquid to give up heat on solidifying. When the substance is all solid the system has lost a phase and become univariant (condensed) again. The temperature may then alter, and so the cooling curve continues substantially as before, reaching the solidification temperature.<sup>1</sup>

When a cooling system has a phase reaction, e.g. from one phase to two phases, but not such as to make it invariant, there is a change in the rate of cooling so that the cooling curve becomes less steep but not horizontal. This change of slope may occur several times. For example, in a ternary system, if the original system is liquid, then there are three degrees of freedom,

$$\begin{aligned} F + P &= C + 1 \\ F + 1 &= 3 + 1. \end{aligned}$$

The first change in rate of cooling will occur when one pure salt begins to deposit as solid. There are then two degrees of freedom. The second change will be when a second salt begins to deposit with the first. There is then one degree of freedom. The third change will be when the eutectic point of the whole system is reached, three solid phases are being deposited (e.g. ice and two salts), and there is no degree of freedom (system is invariant condensed) so long as a liquid phase remains to make four phases in all. The third change is, therefore, to the horizontal on the cooling curve.

An example from binary system will indicate the use of the cooling curve. If a solution of ammonium sulphate as represented by the point *P* on Fig. 1, that is 47.3% ammonium sulphate and at 80° C., is cooled, there will be an arrest in the rate of cooling at 65° C. represented by the point *Q*. This reduced rate of cooling will continue until the temperature reaches — 19° C.,<sup>2</sup> the eutectic temperature, *A*, when the temperature will remain constant, the cooling curve being horizontal, until the whole mixture has become solid. The cooling curve will then continue as in the first part. It will be clear to the reader that this is a means of obtaining sufficient data to plot the phase diagram, Fig. 1.

A brief reference was made to the cooling curve of a solution of ammonium sulphate on p. 11 and the cooling curve was Fig. 1*a*. The curve *AB* is the normal cooling of the solution when there is no phase reaction. At *B* ammonium sulphate begins to crystallize out and this continues until *C* is reached, when the whole mixture begins to solidify. From *C* to *D* both ice and ammonium sulphate are being formed in the solid phase, and at *D* there is no liquid left. Thus, from *D* to *E* no phase reaction is taking place and the cooling is unhindered again. *B* corresponds with point *Q* of Fig. 1 and *C* gives the eutectic temperature.

Special attention must be called to the case of retrograde solubility, as illustrated in Fig. 5, for ferrous sulphate and water. In this case, if a mixture 30% FeSO<sub>4</sub> and 70% water

<sup>1</sup> I.e. in accordance with Newton's Law of Cooling. The difference between the first part and the last is only that due to the replacement of convective cooling in the liquid by diffusive cooling in the solid.

<sup>2</sup> In this case the cooling would be effected by the use of a refrigerant in the outer vessel.

is taken at  $90^{\circ}\text{C.}$ , it will contain solid  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and solution. On cooling, the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  will be dissolved and, as the solubility is retrograde, the act of solution will be exothermic. Thus heat will be liberated and the rate of cooling will be retarded until the temperature reaches the saturation temperature for  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ . Below this temperature there is only one phase (all liquid) and no phase reaction is taking place, so the cooling continues without hindrance, i.e. the cooling curve becomes steeper. On reaching the temperature of a saturated solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  the exothermic deposition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  again retards the rate of cooling, and the cooling proceeds as described for ammonium sulphate.

A typical experimental method for plotting the cooling curve is to take the sample of known composition in a glass boiling-tube, say 6 inches by 1 inch. A thermometer graduated in tenth degrees is fixed in the tube and a stirrer is used. The sample is heated in the tube until it is all liquid. The tube is then placed away from air currents, e.g. in an outer vessel, so that it may radiate heat uniformly. The temperature is noted at one-minute intervals. Supercooling may be avoided by seeding the solution; in any case, if supercooling does occur there will usually be a rise in temperature and the correct point can be determined graphically.

This method for determining transition points is known as *thermal analysis*. Since the results give a temperature for a fixed composition it is obvious that they are more suited for plotting on a polytherm than on an isotherm. For this reason the method is eminently suitable for the binary diagrams which have been given as polytherms. For the ternary and higher systems, which in this book are given as isotherms, the method of thermal analysis would give intermediate isothermal points. The specific temperature points required could then be determined graphically by interpolation.

A particular use of thermal analysis is where two isotherms are being studied on the assumption that there has been no sudden change at intermediate temperatures. The cooling curves of carefully chosen mixtures will show whether this assumption is correct. If a transition is found then we know that an intermediate isotherm must be determined.

**Notes on Three- and Four-Component Systems.** Three-component systems of two salts and water have been described at some length because more complicated systems are largely made up of a number of them. Thus, if the three-component system is understood, the more complicated systems present little difficulty. For example, a four-component system of three salts and water can be divided into three systems each of two salts and water represented on three equilateral triangles. If these three equilateral triangles are arranged in space so that the water corner of each meets to form an apex, the three triangles will stand on a base which is also an equilateral triangle. The solid figure formed is a tetrahedron.

Just as an equilateral triangle was subdivided into a lattice to form the triple co-ordinate graph paper, so a tetrahedron may be imagined as latticed *in space*. Any mixture of three salts and water expressed as percentages may be represented by a point within the tetrahedron, the lattice serving to fix the point and to define its composition.

The three systems on three of the faces of the tetrahedron, the external systems, will each have a three-component invariant point (i.e. when the systems are of the simplest type without hydrates or double compounds). Within the tetrahedron there will be a four-component invariant point representing a solution saturated with respect to all three salts, and from this point three curves will radiate to meet the three three-component invariant points of the external systems.

A simple model will help at this stage, and six matchsticks can be joined together

with sealing wax to form a small tetrahedron. Water will be represented at the apex and the three salts at the three corners of the base. Systems could be represented by making complete models in wire, and this is sometimes done, but it is not generally necessary as one or more projections of the tetrahedron may be drawn. If the small matchstick model is allowed to cast its shadow from a not too near light on to a sheet of paper, the form that the different projections take is readily seen. The drawing of such projections, including the projection of the curves and lines forming the internal system, is only a matter of simple geometry. An article on the projection of the tetrahedron for phase rule study was published in *Z. physik, Chem.*, 1909, **65**, 562.

As the number of components increases the difficulty of graphical representation also increases, because with each additional component an additional dimension is required. For example, a three-component isotherm can be completely represented in two dimensions on triple co-ordinate graph paper. A four-component isotherm needs three dimensions, the tetrahedron. In the same way a five-component isotherm, such as four salts and water, would require four dimensions. The difficulty is overcome by eliminating one of the components, in this case water, as will be shown later in this book.

To revert to the four-component system the tetrahedron lattice is used where the three salts have a common ion. There is another and very important type of four-component system which may be considered as being built up from *four* three-component systems represented on four equilateral triangles. These are arranged in space to form a pyramid on a square base, water being at the apex and the four triangular sides forming the external systems. It is this type of four-component system which is the subject of the next four chapters, because it has so much wider application than the systems where the three salts have a common ion.

**Solid Solution.** Before leaving the three-component system it may be as well to point out that the interpretation of the isotherms is not always as straightforward as the reader has been led to believe. The statements are true in a general sense, but there are some important exceptions. It is beyond the scope of this book to deal with the subject of solid solutions, that is solid phases of variable composition, but it is necessary to mention their existence.

The term solid solution was introduced by van't Hoff, and to-day solid solutions are sometimes referred to as mixed crystals. Roozeboom, at the end of the last century, deduced five possible types of solid solution in systems of two salts and water. Three of the types were when the two salts were completely miscible, and two types when the two salts were only partly miscible but two series of solid solutions were formed, that is one salt dissolved in the other and the other in the former. Since then a sixth type has been recognized where only one series of solid solution is formed, the solid solution being of the nature of a double salt but of varying composition with the varying composition of the liquid solution with which it is in equilibrium. This sixth type was first mentioned by John E. Ricci, (*J.A.C.S.*, 1935, 575).

Two cases of solid solution in systems of two salts and water are shown in Fig. 21 plotted from the data in Tables 21A and 21B. Fig. 21A is a case when the miscibility of the two salts is complete: the curves representing solutions in equilibrium with the pure salts have shrunk to zero and the invariant point has extended into a curve in equilibrium with a solid solution of the two salts, the composition of which varies with the composition of the liquid solution. Fig. 21B is an example given by Ricci (*loc. cit.*): there are two pure solid phases each with its curve representing solution in equilibrium with pure solid.

TABLE 21A  
AMMONIUM SULPHATE.POTASSIUM SULPHATE.WATER  
(From Weston, *J. Chem. Soc.*, 1922, **121**, 1223)

Composition of saturated solutions at 30° C.

Liquid Phase.		Solid Phase.	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . %	K <sub>2</sub> SO <sub>4</sub> . %	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . %	K <sub>2</sub> SO <sub>4</sub> . %
44.2	0	100	0
42.7	1.2	96.7	3.3
40.9	2.4	87.8	12.2
37.8	4.1	71.3	28.7
33.5	5.9	56.4	43.6
31.0	6.4	38.7	61.3
18.5	9.1	25.8	74.2
8.4	10.7	1.8	98.2
0	11.12	0	100

TABLE 21B  
SODIUM SULPHATE.SODIUM BROMATE.WATER  
(From Ricci, *J.A.C.S.*, 1935, **57**, 805)  
Composition of saturated solutions and complexes at 45° C.

Saturated Solution % by weight		Original Complex % by weight		Solid Phase.
Na <sub>2</sub> SO <sub>4</sub> .	NaBrO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	NaBrO <sub>3</sub> .	
32.07	0	—	0	Na <sub>2</sub> SO <sub>4</sub>
30.35	3.12	44.45	2.51	"
29.18	5.64	42.41	4.61	"
28.78	6.32	—	—	Na <sub>2</sub> SO <sub>4</sub> + solid solution
27.76	7.53	37.43	7.00	Solid solution
25.85	10.12	38.96	9.51	" "
22.92	14.38	36.97	13.52	" "
21.58	15.96	32.12	16.28	" "
20.94	17.00	34.95	17.17	" "
20.86	17.17	—	—	Solid solution + NaBrO <sub>3</sub>
19.81	17.93	16.68	30.99	NaBrO <sub>3</sub>
16.54	20.38	14.17	31.98	"
8.10	27.14	6.49	41.96	"
0	34.22	0	—	"

There is a third curve in equilibrium with the solid solution, but the solid solution is not a double salt; it has a composition which varies with the varying composition of the liquid solution. There are two isothermal invariant points representing two solutions, one in equilibrium with one pure solid and the other in equilibrium with the other pure solid. Both solutions are in equilibrium with the solid solution.

The fact that solid solutions are fairly common has led to a school of thought which suggests that all solid phases are solid solutions, even if to an extent too small to be detected

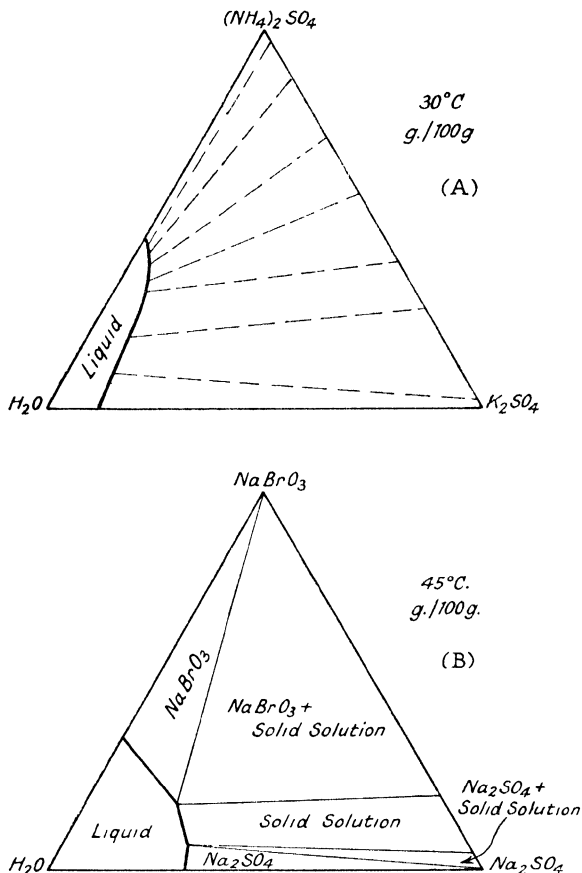


FIG. 21.

by analysis. This idea has no doubt been influenced by the fact that it is impossible to prepare a pure substance. The idea of universal solid solution is supported by A. C. D. Rivett in his book, *The Phase Rule and the Study of Heterogeneous Equilibria*, 1923 (Oxford University Press); he suggests that in a system of one salt and water, the salt cannot be pure at all temperatures because, for a change in composition of the solution phase, there must be a change in composition of the solid phase. On the other hand, Ricci (*loc. cit.*) has very correctly pointed out that phase concentrations are not really percentage by weight, although it is very convenient to consider them so. They are really in terms of mass per unit volume and therefore even a pure solid phase can change its composition with change of temperature. All substances change in volume with change of temperature and, taking mass as constant, the mass per unit volume changes.

The phase rule, as theory, is not concerned with the purity but with the number of

the phases in relation to the number of components and certain variables such as temperature, pressure and concentration. Throughout this book solid solutions have been assumed not to exist except in those cases where they have been found by experiment and the examples used in the various diagrams have been chosen, as far as possible, from the cases where solid solutions have not been found. (There is one exception, glaserite does dissolve some sodium sulphate, so the composition of glaserite varies slightly.)

## CHAPTER VIII

### THE RECIPROCAL SALT PAIR

The four-component system, where the three salts have a common ion, has been mentioned towards the end of the preceding chapter as being represented on a tetrahedron lattice. It was there pointed out that a more important type of four-component system is one which requires to be represented by a pyramid on a square base, water being represented at the apex. This is the system of two salts and water where the two salts do not have a common ion. It has been emphasized that, for the three-component systems to be represented on triple co-ordinates, the two salts must have a common ion. This is because, when the two salts do not have a common ion, there may be chemical reaction between the two salts to produce two other salts.

For example, sodium sulphate and potassium chloride may react to produce sodium chloride and potassium sulphate. This reaction is known as double decomposition, and the four salts involved are called a reciprocal salt pair. Lowenherz in 1894 and van't Hoff in 1895 were the first to work on this aspect of phase theory. For other early references see Meyerhoffer and Saunders, *Z. physik. Chem.*, 1899, **28**, 453, and 1899, **31**, 370.

If the amounts of the first two are in chemical equivalent proportion, then the composition may be expressed in terms of either the first pair or the second pair. If, however, there is an excess of one of the first pair, then the composition may be expressed either in terms of the first pair or in terms of the second pair with an excess of one of the first pair, making three salts and water instead of two salts and water. Thus, although in the reciprocal salt pair *four* salts are involved, any mixture of the four salts can be expressed in terms of three of them, and such a system therefore becomes a four-component system of *three* salts and water. Such a system, however, cannot be represented on the tetrahedron, because this does not allow all the four salts to be represented. It is for this reason that the *square*-based pyramid is used, water being at the apex, and one of the four salts at each of the corners. The salts of each pair must be diagonally opposite and not adjacent.

**The Base of the Pyramid.** Before proceeding to study the pyramid as a solid figure it may be well to make a study of its base, as a plane figure. The base of the pyramid represents mixtures of the salts without any water and in order to have a square base, instead of an irregular quadrilateral, the composition of a mixture must be expressed in chemical equivalents because it has to satisfy a chemical equation.

For example :

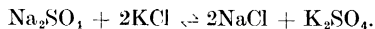


Fig. 22 represents the base of a pyramid, each corner not only representing a pure salt but implying a definite quantity of that salt, that is, one chemical equivalent. It may for convenience represent 100 chemical equivalents. According to the above equation one molecule of sodium sulphate is equivalent to two molecules of potassium chloride, and therefore the corner of the diagram for potassium chloride implies a double molecule ( $\text{K}_2\text{Cl}_2$ ). It is customary to refer to these quantities as mols, and for convenience the double molecule of potassium chloride is always referred to as a mol. In other words, by a mol, in this case, is meant the quantity of a chemical which will satisfy the equation whether this be one, two or more molecules. One example will make this quite clear.



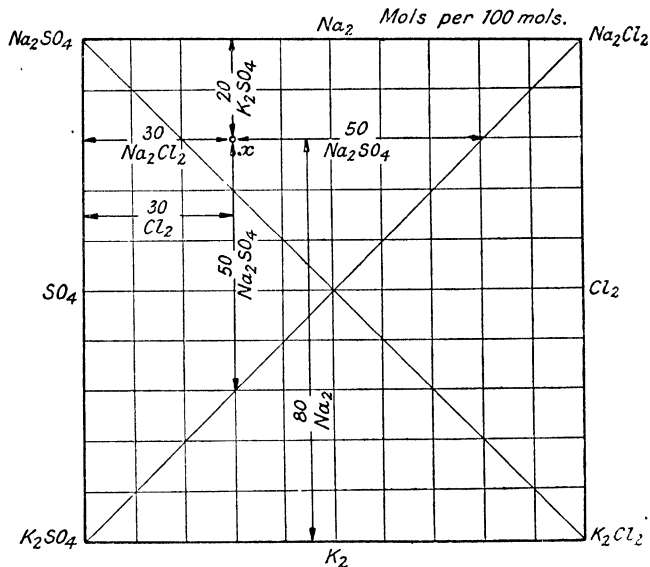


FIG. 22.

Suppose a mixture contains :

Sodium sulphate . . . . .	50.5%
Sodium chloride . . . . .	24.9%
Potassium sulphate . . . . .	24.6%

To convert to mols it is necessary to divide the percentages by their respective molecular weights which are :

$\text{Na}_2\text{SO}_4$ . . . . .	142
$\text{Na}_2\text{Cl}_2$ . . . . .	117
$\text{K}_2\text{SO}_4$ . . . . .	174

This gives

$\text{Na}_2\text{SO}_4$ . . . . .	0.357 mols
$\text{Na}_2\text{Cl}_2$ . . . . .	0.213 „
$\text{K}_2\text{SO}_4$ . . . . .	0.141 „

in 0.711 „ of mixture.

Thus, 100 mols of mixture contain :

$\text{Na}_2\text{SO}_4$ . . . . .	50 mols
$\text{Na}_2\text{Cl}_2$ . . . . .	30 „
$\text{K}_2\text{SO}_4$ . . . . .	20 „

In order to plot this on Fig. 22 the corners are taken as each representing 100 mols of the pure substance, any point within the diagram representing 100 mols of mixture. Since

any mixture of the four possible salts can be expressed in terms of three salts, any point in the square may be regarded as being in a right-angled triangle, or half a square. The point representing the mixture given above is in the triangle  $K_2SO_4$ . $Na_2SO_4$ . $Na_2Cl_2$ . Only two figures are required to fix the position of the point, and it is most convenient to take the figures for the salts at opposite ends of a diagonal, that is in this case  $Na_2Cl_2$  and  $K_2SO_4$ . In other words, the salt at the right angle of the triangle is ignored. The point representing the mixture is marked  $x$  on Fig. 22, this being 30 divisions towards  $Na_2Cl_2$  and 20 divisions towards  $K_2SO_4$ , the corner  $Na_2SO_4$  being the origin.

It will be seen that the amount of the third component,  $Na_2SO_4$ , is the distance from  $x$  to the diagonal, all measurements being *parallel to the sides of the square*.

With reciprocal salt pairs it is not always known which three salts result from a mixture. For instance, in the case under consideration, point  $x$  of Fig. 22, the composition could have been expressed in terms of sodium sulphate, sodium chloride and potassium chloride instead of potassium sulphate, sodium sulphate and sodium chloride. It will be noticed that  $x$  is in both these triangles. For this reason it is a common practice to express the composition of a mixture in terms of the radicals,  $Na_2$ ,  $Cl_2$ ,  $K_2$  and  $SO_4$ . The above mixture will be seen to contain :

$Na_2$	80	mols from	$Na_2SO_4$	(50) and	$Na_2Cl_2$	(30)
$K_2$	20	„ „	$K_2SO_4$			
$Cl_2$	30	„ „	$Na_2Cl_2$			
$SO_4$	70	„ „	$Na_2SO_4$	(50) and	$K_2SO_4$	(20).

It will be noted that the basic radicals,  $Na_2$  and  $K_2$ , total 100, and in the same way the acid radicals,  $Cl_2$  and  $SO_4$ , total 100. Any pair of figures is sufficient to determine the point, the pair being of opposite type of radical, that is, one basic and one acid. In the example  $Na$  or  $K$  might be taken with  $Cl$  or  $SO_4$ .

In the square the line between the corners marked  $Na_2SO_4$  and  $Na_2Cl_2$  represents 100 mols of  $Na_2$ ; the line between  $Na_2Cl$  and  $K_2Cl_2$  represents 100 mols of  $Cl_2$  and the other lines similarly represent  $K_2$  and  $SO_4$  as marked on Fig. 22. Thus to plot the point  $x$ , this is 30 divisions towards the  $Cl_2$  and 80 divisions towards the  $Na_2$ , all measurements being parallel to the sides of the square. In this case the diagonal is ignored.

**Plotting a Point within the Pyramid.** Passing from the base to the whole pyramid water is taken as being at the apex, the base representing mixtures which contain no water. Water is therefore measured upwards, 10 mols of water per 100 mols of mixture being on a plane parallel to the base and 10 divisions above it. Similarly, a mixture with 80 mols of water per 100 mols of mixture is represented on a plane parallel to the base 80 divisions above it.

As an example take a mixture containing :

Sodium sulphate . . . .	15.85%
Sodium chloride . . . .	26.15%
Potassium chloride . . . .	49.95%
Water . . . . .	8.05%.



dimensional model of the pyramid. In practice, projections are used as far as possible. Fig. 23 can now be considered as such a projection. It is not drawn in perspective, as in that case the sides of the base would not be parallel, and measurement would be more difficult. The base is drawn as a parallelogram and this gives two scales for measurement. The line  $\text{K}_2\text{Cl}_2.\text{Na}_2\text{Cl}_2$  and the line  $\text{K}_2\text{SO}_4.\text{Na}_2\text{SO}_4$  are of equal length and are considered as being divided into 100 equal parts. This scale is used for all measurements in any part of the figure where those measurements are parallel to the lines named.

The second scale is obtained by dividing the lines  $\text{K}_2\text{SO}_4.\text{K}_2\text{Cl}_2$  or  $\text{Na}_2\text{SO}_4.\text{Na}_2\text{Cl}_2$  into 100 equal parts, and this scale is used for all measurements parallel to these lines.

A third scale, the measurement of water from the base, is less definite on the projection. Any or all of the four edges radiating from the apex can be divided into 100 parts, but these edges are not of equal length on the projection. In measuring, the water measurements are made from one of the edges and the scale of that edge must be used. For example, in plotting the point  $y$  the procedure would be as follows:

From  $\text{Na}_2\text{Cl}_2$  measure 40 mols of water along the edge  $\text{H}_2\text{O}.\text{Na}_2\text{Cl}_2$  in terms of the scale of that edge. This gives the point  $A$ , which is four-tenths of that line.

From the point  $A$  measure 30 mols of potassium chloride on a line parallel to the line  $\text{Na}_2\text{Cl}_2.\text{K}_2\text{Cl}_2$  and in the scale of that line. This gives the point  $B$ .

From the point  $A$  also measure 10 mols of sodium sulphate on a line parallel to the line  $\text{Na}_2\text{Cl}_2.\text{Na}_2\text{SO}_4$  and in the scale of that line. This gives the point  $C$ .

From  $B$  and  $C$  complete the parallelogram to give  $y$ .

It should be noted that it is not necessary to draw the 40 mol % water plane, nor is it even necessary to draw the complete parallelogram  $AByC$ . The point can be obtained by drawing two lines only, as is shown in the next example.

Let the mixture be:

Sodium sulphate . . . . .	20	mols	%
Sodium chloride . . . . .	25	„	„
Potassium chloride . . . . .	30	„	„
Water . . . . .	25	„	„

As before, measure 25 mols of water along the edge. This gives the point  $D$ .

From  $D$  measure 30 mols potassium chloride parallel to the line  $\text{Na}_2\text{Cl}_2.\text{K}_2\text{Cl}_2$ , giving the point  $E$ .

From  $E$  measure 20 mols sodium sulphate parallel to the line  $\text{Na}_2\text{Cl}_2.\text{Na}_2\text{SO}_4$ , giving the point  $z$  which represents the mixture.

Having plotted a point on a projection it will be realized that, if the construction lines are removed, it is not possible to "read back" the composition of the point, because all points within the solid figure on a straight line in the direction of projection are represented by only one point on the projection. In order to be able to say exactly where a point is it is necessary to have two projections such as a plan and an elevation. The elevation gives two of the dimensions and the plan gives the third, or vice versa.

In order to avoid the necessity and trouble of drawing two figures it is a common practice to treat the base of the pyramid on the oblique elevation projection of Fig 23 as if it were a plan. Points within the solid pyramid are then projected on to this base. In other words, when  $y$ , for example, is plotted on the elevation, its projection is also plotted on the base of the same diagram. The latter is usually carried out by calculating

the mol % of the salts on the total salt content. That is the figures used are those for the mixture which would be obtained if all water was removed.

To take the example already given for the point  $y$  the composition of the mixture is :

Sodium sulphate . . . .	10	mols %
Sodium chloride . . . .	20	" "
Potassium chloride . . . .	30	" "
Water . . . . .	40	" "

If the water is removed 60 mols of salt will be left, and this brought to mol percentage on the dry salts gives a composition :

Sodium sulphate . . . .	16.7	mols %
Sodium chloride . . . .	33.3	" "
Potassium chloride . . . .	50.0	" "

This is plotted on the base by measuring 50 mols of potassium chloride along the  $\text{Na}_2\text{Cl}_2\text{--K}_2\text{Cl}_2$  line to give  $F$ , and measuring 16.7 mols of sodium sulphate from  $F$  along a line parallel to the  $\text{Na}_2\text{Cl}_2\text{--Na}_2\text{SO}_4$  line. The point thus obtained is marked  $y'$ , and is the point  $y$  projected from the water apex on to the base. It is the shadow of  $y$  which would be cast on the base by a point of light at the apex. Thus, if a line is drawn from  $y'$  to the apex it will pass through  $y$ .

If now the construction lines are removed and we are told that  $y$  is the point representing the mixture and that  $y'$  is its projection *on the base*, it is possible to read the composition of  $y$  from the figure. The position of  $y'$  on the base gives the ratio of the three salts to one another. This is read by taking the base as being Fig. 22, distorted into a parallelogram. The relative position of  $y'$  and  $y$  to the water apex gives the ratio of water to salt mixture. From these two ratios the absolute composition may be calculated, as will be shown at a later stage.

**The Phase Diagram within the Pyramid.** The simplest way to understand the phase diagram for a reciprocal salt pair is to pass directly to a diagram. In order to have a figure which can be used to illustrate all the various points which have to be considered, and one in which the lines are so placed as to make explanation easy, we have taken an imaginary salt pair, a chloride and nitrate of the fictitious metals  $X$  and  $Y$ . The reaction is thus :

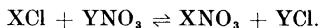


Table 22 gives the figures in mols % from which the diagram, Fig. 24, has been plotted.

The points  $K$ ,  $A$  and  $L$  are on one face of the pyramid, which is an equilateral triangle. They are, therefore, plotted on the triangle water.YCl.XCl exactly as was described in Chapter IV for the two salts and water diagrams. The fact that on the projection the triangle is not equilateral makes no difference, as each side is considered as being divided into 100 parts to give the lattice. For a more accurate diagram there would be further points between  $K$  and  $A$ , and between  $L$  and  $A$ , but these have been omitted for simplicity.

The three other triangular faces form similar systems. Thus there are four external systems of two salts and water. The points  $K$ ,  $L$ ,  $M$  and  $N$  represent the solubility of single salts in water. The points  $A$ ,  $B$ ,  $C$  and  $D$  are the equilibrium points of two salts and water, and each triangular face is completed by drawing the curves and lines as for the three-component systems.

TABLE 22  
THE QUATERNARY SYSTEM.  $\text{XCl} \cdot \text{YNO}_3 \cdot \text{Water}$   
RECIPROCAL SALT PAIR

Mols per 100 Mols of Solution						Solid Phase.
Point.	XCl.	YCl.	$\text{XNO}_3$	$\text{YNO}_3$	Water	
<i>K</i>	—	30.5	—	—	69.5	YCl
<i>L</i>	41.0	—	—	—	59.0	XCl
<i>M</i>	—	—	56.0	—	44.0	$\text{XNO}_3$
<i>N</i>	—	—	—	44.0	56.0	$\text{YNO}_3$
<i>A</i>	25.25	21.25	—	—	53.5	XCl + YCl
<i>B</i>	13.45	—	41.05	—	45.5	XCl + $\text{XNO}_3$
<i>C</i>	—	—	38.7	19.3	42.0	$\text{XNO}_3 + \text{YNO}_3$
<i>D</i>	—	21.8	—	24.7	53.5	YCl + $\text{YNO}_3$
<i>E</i>	22.2	—	3.2	30.1	44.5	XCl + $\text{YNO}_3$ + YCl
<i>F</i>	10.6	—	26.7	21.2	41.5	XCl + $\text{YNO}_3$ + $\text{XNO}_3$
<i>H</i>	18.02	—	10.47	4.26	67.25	Unsaturated
<i>O</i>	26.70	—	15.50	6.30	51.50	Saturated XCl
<i>P</i>	38.70	—	22.55	9.15	29.60	XCl, saturated $\text{XNO}_3$
<i>T</i>	44.0	—	25.60	10.40	20.00	XCl + $\text{XNO}_3$ sat. $\text{YNO}_3$
<i>Q</i>	55.0	—	32.0	13.0	0	Dried up

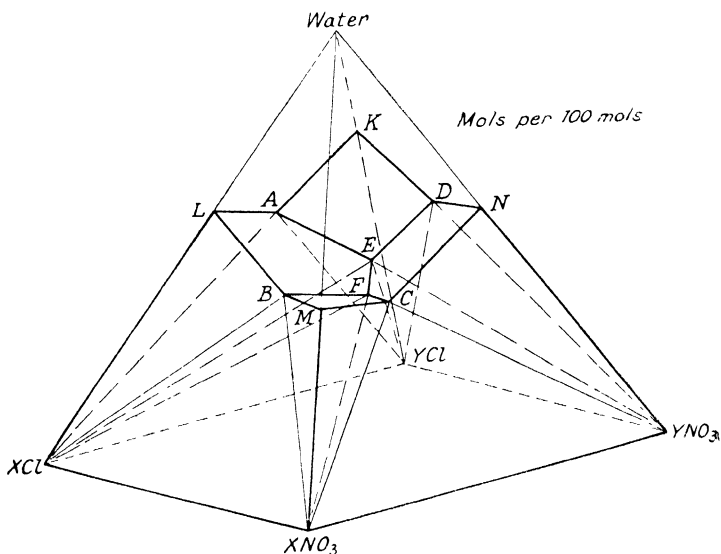


FIG. 24.

The other two important points  $E$  and  $F$  are within the pyramid and are plotted as described earlier in this chapter for Fig. 23. These two points represent solutions which are saturated with three salts, as indicated in column 7 of the table. Curves are then drawn from  $E$  to  $A$  and  $D$  and from  $F$  to  $B$  and  $C$ , that is from the points of three salts to the points representing solutions saturated with only two of them. Finally the curve  $EF$  is drawn. As with the curves on the faces, so with these curves, there should have been intermediate plotting points.

To complete the internal system straight lines are drawn from  $E$  and  $F$  to the corners representing the three salts with which each is saturated. It will now be seen that each point that has been plotted is joined by a straight line or lines to the salt or salts with which the solution is saturated. Thus the number of straight lines from a point towards the base shows the number of salts with which the solution is in equilibrium. For example, from  $K$  there is only one line: to  $YCl$ . From  $A$  there are two lines: to  $YCl$  and  $XCl$ . From  $E$  there are three lines: to  $YCl$ ,  $XCl$  and  $YNO_3$ .

In Fig. 24 the curves which have just been described are represented by heavy lines to distinguish them from the rest of the diagram. These curves form four irregular and curved surfaces which cut the pyramid into two parts. The part of the pyramid above the surfaces could be removed in one piece and represents "all liquid," with pure water at the apex. The part below the surfaces is complex, being mixture of solid and liquid. The surfaces themselves represent solutions which, although being liquid, are saturated with respect to one or more salts.

In a simple phase diagram of two salts and water there are two curves each representing solutions saturated with one salt and containing varying amounts of the other. In systems of three salts and water the curves have been extended into *surfaces*, which in the same way represent solutions saturated with one salt but containing varying amounts of the other two. For example, any point on the surface  $KAED$  represents a solution saturated with  $YCl$  and containing some  $XCl$  and  $YNO_3$ , but not sufficient for saturation.

Where two surfaces meet they form a *curve* representing solutions saturated with two salts but containing varying amounts of the third. For example, a point on the curve  $AE$  represents a solution saturated with  $YCl$  and  $XCl$ , and containing some  $YNO_3$ . The curve  $EF$  differs somewhat from the other curves; it represents solutions saturated with two salts, in this case  $XCl$  and  $YNO_3$ , but containing varying amounts of a third salt  $XNO_3$ . The third salt might have been  $YCl$  if the curve  $EF$  had been the other side of a vertical plane on the diagonal  $XCl.YNO_3$ . (Consult Fig. 28.)

Where three surfaces meet a *point* is formed representing a solution saturated with THREE salts and containing no other salt. This point is called a quaternary invariant point if the temperature is fixed. Thus the point  $F$  represents a solution saturated with the three salts  $XCl$ ,  $XNO_3$  and  $YNO_3$ .

In order to explain the part of the pyramid below the saturation surfaces, Figs. 25, 26 and 27 have been drawn, dissecting this part of the pyramid into eleven solid figures. Each of these solid figures is a "field" within the meaning given to that term in earlier chapters. For instance, in phase diagrams represented in two dimensions the fields are planes. With three-dimensional diagrams the fields become figures in space.

The eleven fields can be grouped into three types. Each field represents solution and solid, but the solid may be one pure salt, a mixture of two salts or a mixture of three salts.

Fig. 25 illustrates the four fields of one solid salt and solution. This figure should be compared with Fig. 24 in order to recognize where the fields lie in the pyramids. Each

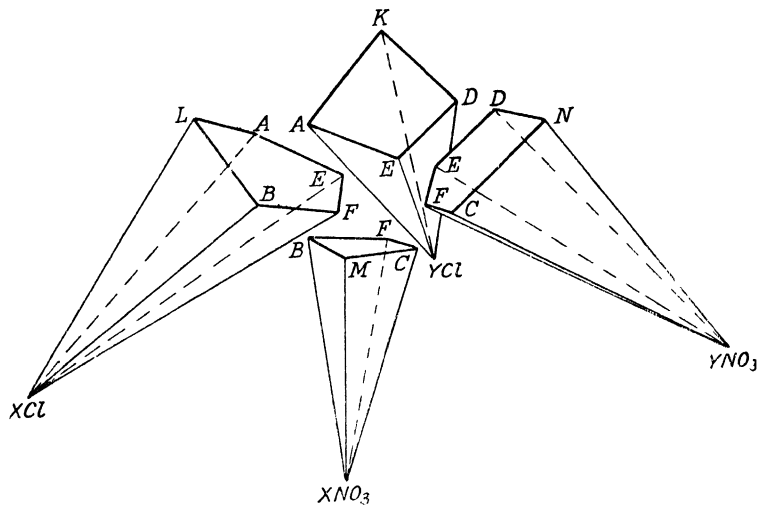


FIG. 25.

field is a pyramid radiating from one of the corners of the square base. The extent of the field is limited by the saturation surface. Any complex within one of these four fields consists of a solution and one of the pure salts in the solid state. The composition of the salt is denoted by the corner from which the field radiates, and the composition of the solution is found by drawing a straight line in space from the known solid through the complex to meet the saturation surface at the solution point. It should be noted that the surfaces from the corner on the inside face of these cones are curved and not plane.

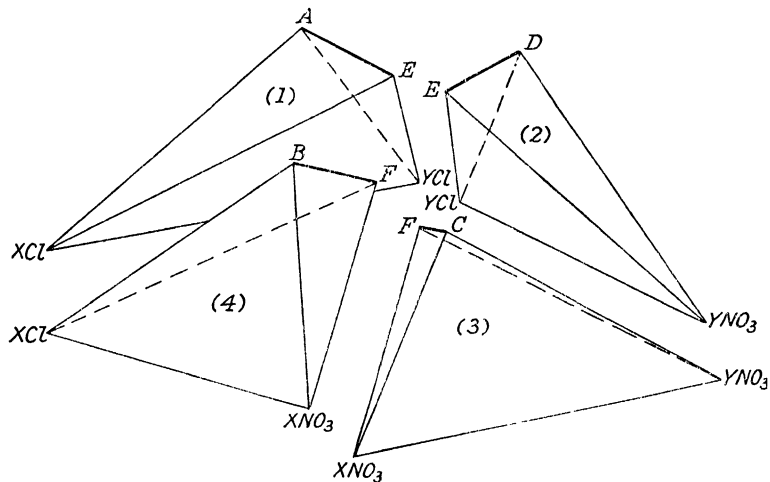


FIG. 26.



There are five fields of the second type, two solid salts and solution. Four of these fields are illustrated in Fig. 26 and the fifth is the central field No. 6 in Fig. 27, each field forming an irregular tetrahedron. In this case neither the solid nor the solution is of fixed composition. A complex within one of the fields consists of a mixture of two solid salts on the line joining the two salts, and a solution on the solution curve. For example, a complex within field 1 of Fig. 26 has for its solid phase a mixture of  $YCl$  and  $XCl$ , its composition being somewhere on the line joining these two salts. Its solution has a com-

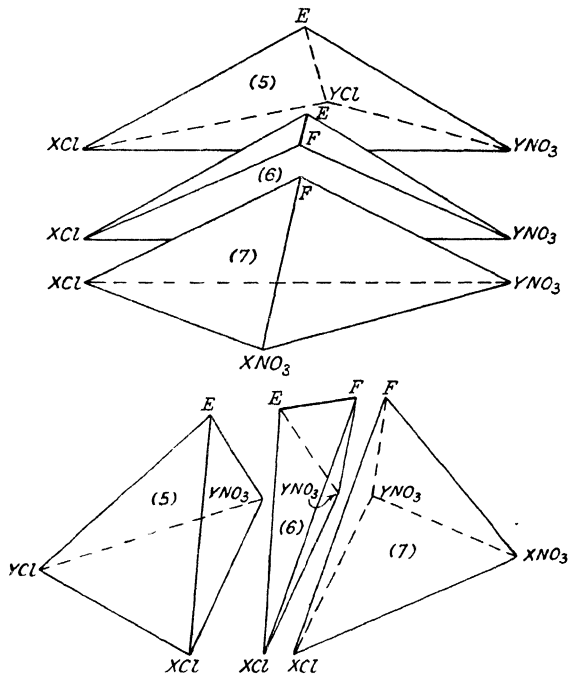


FIG. 27.

position somewhere on the curve  $AE$ . In this case it is not possible to determine the composition of solution or solid by drawing a line through the complex because there is no other known point. The compositions of the solid and the solution can, however, be determined on a diagram by constructing the plane on the line  $YCl.XCl$  which passes through the complex point. The point where this plane cuts the curve  $AE$  represents the solution point, and a straight line from the solution point back through the complex point will meet the line  $YCl.XCl$  at the point representing the composition of the solid phase.

The four fields in Fig. 26 are related to the four sides of the square base. The fifth field of this type, in Fig. 27, is related to one of the diagonals of the square. A sixth field of the same type on the other diagonal is not possible. A glance at Fig. 24 shows that the saturation surfaces belonging to  $YCl$  and  $XNO_3$  are separated by the distance  $EF$ . This implies that these two salts cannot co-exist in the solid state in equilibrium with solution,



orthogonal projection of the same space model, but in this case it is a plan. It is the view looking down into the crate which the saturation surfaces make in the pyramid. These surfaces are denoted by the same letters as in Fig. 24 and they should be readily recognized.

Water is at the centre of the figure, the four salts being at the corners of the square. The two diagonals divide the figure into four triangles which represent the triangular surfaces of the pyramid. Taking one triangle as an example, the curves  $KA$  and  $AL$  are on the surface of the pyramid, so that the triangle with the two curves mentioned forms a system of two salts and water. The other three triangles are similar, and this disposes of the outside edge of the crater and hence of the four external systems.

Points of the external system are plotted from the centre, taking the length of each half-diagonal as 100 units, and using the figures given in the table without any modification. For example, point *K* is 30.5 divisions from the centre on the diagonal towards YCl, the table giving 30.5 mol % YCl. The point *A* is plotted by measuring 21.25 divisions from the centre along the YCl diagonal (21.25 mol % YCl) and 25.25 divisions parallel to the XCl diagonal (25.25 mol % XCl). The other points of the external system *L*, *B*, *M*, *C*, *N* and *D* are plotted similarly. It will be seen that each of the four small triangular systems is plotted as for triple co-ordinates, bearing in mind that one angle of the triple co-ordinates is a right angle, this being the water corner.

In order to plot the internal system the centre is still taken as the origin and the diagonals used as axes. Unless the complex lies on one of the diagonals there are always three figures, apart from water, given for an internal point. Thus the point *E* is expressed in terms of YCl, XCl and YNO<sub>3</sub>. As there are only two plotting axes, two of these figures must refer to the same axis. In the case of *E*, XCl and YNO<sub>3</sub> are at opposite ends of the same diagonal, the figures being 22.2 mol % XCl and 30.1 mol % YNO<sub>3</sub>. This means that the point *E* is 22.2 divisions from the centre towards XCl and 30.1 divisions towards YNO<sub>3</sub>, the final result being 30.1 - 22.2 = 7.9 divisions towards YNO<sub>3</sub>, this being the greater. It is also 3.2 divisions (3.2 mols % XNO<sub>3</sub>) towards XNO<sub>3</sub>.

Applying the same method to the point  $F$ , this is given in the table as:

26.7	mols	%	XNO <sub>3</sub>
10.6	„	„	XCl
21.2	„	„	YNO <sub>3</sub>

and point is plotted as ‘

$$\begin{array}{l} 21.2 - 10.6 = 10.6 \text{ divisions towards YNO}_3 \\ \text{and } 26.7 \quad \quad \quad \quad \quad \quad \quad \quad \text{XNO}_3. \end{array}$$

As regards reading back the composition of any point on the figure, this is only possible when the point is known to be on the external system. For an internal point two figures only can be read from the figure: the mol percentage of one salt and the difference in mol percentage between the other two. Thus for the point *F*

XNO <sub>3</sub>	can be read as	26·7	mols	%
YNO <sub>3</sub> — XCl	" " " "	10·6	" "	" "

In other words, the same point can represent a number of complexes with different contents of  $\text{YNO}_3$ ,  $\text{XCl}$  and water. At a later stage it will be shown how this difficulty can be overcome.

On the external system there happens to be an imaginary lattice for reading the water :

this is parallel to the sides of the square and makes each triangular side of the pyramid a triple co-ordinate diagram. \*

It should be stated here that some workers prefer to express their data in terms of mols per fixed quantity of water, e.g. 100 g. or 1,000 mols, instead of mols %. Löwenherz used this method for plotting his pyramid and for its orthogonal projection. By this method the water contents of solutions are known but, here again, the composition of points in the internal system cannot be read from the diagram.

To summarize, two different types of projection have been described to represent the reciprocal salt pair: the pictorial projection of the whole pyramid (Fig. 24), and its orthogonal projection in plan (Fig. 28). The phase diagram, that is the *three-dimensional* figure, obeys the same rules as already given for triple co-ordinate diagrams. To give two examples only, removal of water moves the complex in a straight line away from the point representing water; the proportion of liquid to solid in a complex is found by measuring the line drawn from the solid point to the complex point and from the complex point to the solution point. If a suitable three-dimensional figure were available there would be little difficulty in applying the rules to practical examples, but there are certain limitations in working with projections. An example of the use of such projections in practice is the subject of the next chapter.

## CHAPTER IX

### SALT PAIR DIAGRAM APPLIED TO EVAPORATION

It is now proposed to work out one operation, evaporation of water, to show how a projection such as Fig. 24 can be used, although, as will be seen in the next chapter, we do not recommend this method.

**Pictorial Projection for Evaporation of Water.** Accurate plotting and measurement of the internal systems on a pictorial projection is difficult and tedious. In Fig. 24, for example, the edges are of various lengths which necessitates the use of different scales which, to say the least, is unsatisfactory and liable to error. Again, an internal point cannot be read back without some additional information and this limits the use of such a diagram. Although Fig. 24 shows the saturation surfaces well away from the apex this condition is not found generally, with the result that the saturation surfaces are small unless large diagrams are drawn.

All these difficulties can be avoided by the use of simple diagrams developed from projections of the pyramid. The reason, however, for spending time and space on the pictorial projection is that the understanding of phase reactions within the pyramid forms the necessary background for the study of the diagrams developed therefrom.

Fig. 29 is reproduced from Fig. 24 with only one saturation surface drawn. The apex  $W$  represents water and points on any line drawn from  $W$  to the base of the pyramid represent changes in composition of a complex by the removal (or addition) of water. This line will be referred to as the *water line*.

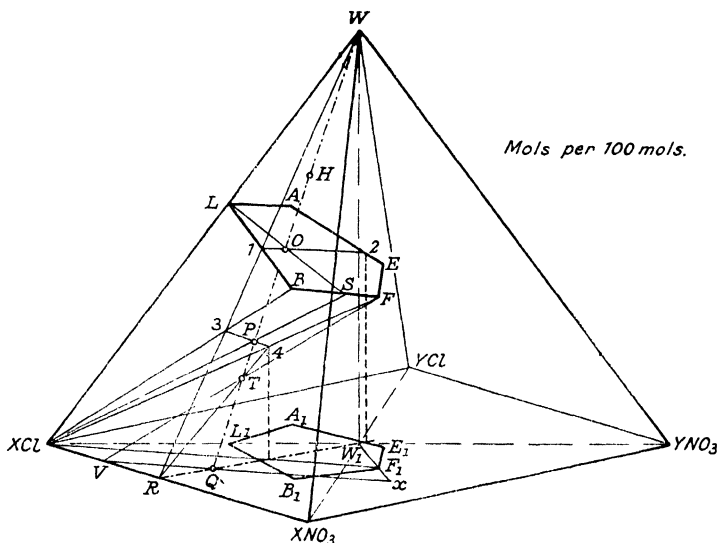


FIG. 29.

The water line chosen,  $WQ$ , passes through four fields: the liquid field and three fields of solid and liquid. Suppose the point  $H$  represents a solution in the liquid field and that water is removed without change of temperature. The complex moves from  $H$ , away from  $W$ , to  $O$  in the liquid field,  $O$  being the intersection of the line with the saturation surface. The movement of the complex continues through the field of  $XCl$  and solution to the point  $P$  where the water line intersects the undersurface of the field. The complex then passes to  $T$  through the field of  $XCl$ ,  $XNO_3$  and solution,  $T$  being on the undersurface of that field. Further evaporation takes the complex towards  $Q$  through the field of  $XCl$ ,  $XNO_3$ ,  $YNO_3$  and solution,  $Q$  representing the composition of the dried-up solution.

When the complex is at  $P$  and the solid phase is  $XCl$  the solution is at  $S$ , this being where the line  $XCl.P$  produced meets the curve  $BF$ . Thus, while the complex is passing from  $O$  to  $P$ , the solution moves from  $O$  to  $S$  along a curve on the saturation surface. Similarly, as the complex moves from  $P$  to  $T$ , the solution moves from  $S$  to  $F$ ; in this case the solid phase has a changing composition moving from  $XCl$  to  $V$ , as explained in dealing with Fig. 26. Further evaporation moves the complex from  $T$  to  $Q$ , but the composition of the solution remains constant at  $F$ , the solid phase moving from  $V$  to  $Q$ . Reference to Figs. 25, 26 and 27 will make the above clear.

To proceed to the quantitative examination of this evaporation problem it is assumed that the composition of  $H$  is given and has been plotted by the method already described. The composition of  $Q$  is readily calculated and also plotted.

	$H$	$Q$
$XCl$ . . . .	18.02	55.0
$YNO_3$ . . . .	4.26	13.0
$XNO_3$ . . . .	10.47	32.0
Water . . . .	67.25	0

The water line is drawn and the other points  $O$ ,  $P$  and  $T$  may be found as follows.

The water line is projected on to the base by drawing a line from the centre of the base,  $W_1$ , through  $Q$  to meet the edge of the base at  $R$ . By drawing the line  $WR$  a vertical plane  $WRW_1$  is obtained. This plane cuts the boundary surfaces between the fields along the lines 1 to 2, 3 to 4 and  $R$  to 4. The points 1, 3 and  $R$  are known because the curve  $LB$  and the lines  $XCl.B$ , and  $WR$  all lie on a surface of the pyramid.

In order to fix the points 2 and 4 the curves  $AE$  and  $EF$  and the line  $F.XCl$  are projected orthogonally on to the base. This means they are plotted from the data in Table 22 by the method described in Chapter VIII for Fig. 28, bearing in mind that the base is distorted. The projected points are lettered  $A_1$ ,  $E_1$  and  $F_1$ . The line  $F_1.XCl$  is now drawn, and this line is a projection of  $FXCl$ . From the point where the line  $RW_1$  produced cuts the curve  $A_1E_1$  draw a vertical<sup>1</sup> line to meet the curve  $AE$  at 2. From the point where the line  $RW_1$  cuts the line  $F_1.XCl$  draw a vertical<sup>1</sup> line to meet the line  $FXCl$  at 4.

The lines 1 to 2, 3 to 4 and  $R$  to 4 cut the water line at  $O$ ,  $P$  and  $T$  respectively. Knowing the position of  $P$  the position of  $S$  is also fixed and, similarly, from  $T$  the position of  $V$  is fixed.

To examine the phase reactions of a complex between  $O$  and  $P$  a line is drawn from  $XCl$  through the complex to give a solution on the curve  $OS$ , the proportion of solution to solid conforming to the general rules. Similarly, for a complex between  $T$  and  $Q$  a line

<sup>1</sup> Vertical in this sense means parallel to  $WW_1$ .

is drawn from the solution  $F$  through the complex to give the composition of the solid phase on the straight line  $VQ$ .

For a complex between  $P$  and  $T$  the method is not so simple because the points representing solid phase and solution are both changing. Consider the triangular plane  $F.XCl.XNO_3$  with the point  $T$  on its surface. If a similar plane were constructed from the line  $XCl.XNO_3$  with its apex at a point between  $S$  and  $F$  representing the composition of the solution, the point where the water line met the plane would represent the composition of the complex. A straight line drawn from the chosen solution (apex) through the complex would meet the edge of the base between  $XCl$  and  $V$  at a point representing the solid phase. The point where the water line meets the plane can be found by the same method as was suggested for finding  $T$ .

The composition of any point between  $H$  and  $Q$  is readily obtained by measuring the ratio. For example, the composition of  $P$  is determined thus.  $WQ$  is taken as 100 units of the complex. Then  $QP$  represents the water and  $WP$  represents the total salts in the complex, these solids having the composition of  $Q$ .

$$\begin{aligned} WQ &= 11.15 \text{ in.}^1 && \text{i.e. 100 units} \\ QP &= 3.35 \text{ in} && \text{i.e. 30.0 mol \% water} \\ WP &= 7.8 \text{ in.} && \text{i.e. 70.0 mol \% salts.} \end{aligned}$$

The composition of  $P$  is therefore readily obtained from the composition of  $Q$  which is already known.

	XCl	YNO <sub>3</sub>	XNO <sub>3</sub>	Water
100 mols $Q$ contain . . . .	55.0	13.0	32.0	0
70.0 mols $Q$ contain . . . .	38.5	9.1	22.4	—
i.e. 100 mols $P$ contain . . . .	38.5	9.1	22.4	30.0

The water removed from  $H$  to give a complex of the composition of  $P$  may also be calculated. In this case  $WP$  is taken to represent the amount of complex  $H$  and then  $PH$  represents the amount of water to be removed.

$$\begin{aligned} WP &= 7.8 \text{ in.}^1 \\ PH &= 4.2 \text{ in.} \end{aligned}$$

Thus 4.2 mols of water is removed from 7.8 mols of solution  $H$ .

Before proceeding to another type of projection it should be noted that the saturation surfaces are curved and so are the surfaces radiating from the curves which divide the saturation surfaces (see Figs. 25, 26, 27). This means that the construction given for the determination of the points  $O$ ,  $P$  and  $S$  demands that certain lines such as 1 to 2, 3 to 4 and  $OS$  should be drawn as curves and not as straight lines. In practice, if the original curves bounding the surfaces are pronounced, the construction curves can be drawn between them with reasonable accuracy. If the original curves are practically straight then the construction lines are made straight.

The point  $T$  does in any case lie on a plane.

**Orthogonal Projection for Evaporation of Water.** The same evaporation problem will now be briefly indicated on the orthogonal projection, Fig. 28. The same points  $H$  and  $Q$  have been taken to represent the solution and the dried-up salts respectively. The water line is  $WHQ$  as before.

<sup>1</sup> These measurements were made on a drawing of Fig. 29 on which the water vertical,  $WW_1$ , was 10 in.

It is obvious that the position  $O$  cannot be found from this diagram alone, but in some problems the composition of a saturated solution is known. Thus, if  $O$  were the starting point instead of  $H$ ,  $P$  may be found as follows.

The line  $LO$  is drawn and produced to meet the curve  $BF$  at  $S$ . This line may be an interpolated curve if necessary. The line  $S.XCl$  is drawn cutting the water line at  $P$ .

$T$  can be found by plotting the drying-up point of solution  $F$  at  $X$ . A line is drawn from  $X$  through  $Q$  to meet the outside edge at  $V$ . A line from  $V$  to  $F$  cuts the water line at  $T$ . A comparison with Fig. 29 will show the reason for this.

The orthogonal plan has similar objections to the pictorial projection and its use for technical problems is limited. It is not, therefore, proposed to spend any more time on these projections but to proceed at once to the recommended method.



## CHAPTER X

### JÄNECKE'S PROJECTION

There is another type of projection, introduced by Prof. Ernst Jänecke<sup>1</sup> of Hanover in 1906, which assumes that a shadow is cast from a point of light situated at the apex of the pyramid. This is still a plan, but the eye, instead of viewing the figure from a distance, is placed at the apex. The four external triangular surfaces are thus reduced to four straight lines which form the boundaries of the projection. Fig. 30 is Jänecke's projection of the space model represented in Fig. 24, and the same lettering is used.

A glance back at Fig. 28 will show that in the new projection the external boundary of the crater *KALBMCND*, has been distorted, and extended so that its outer boundary

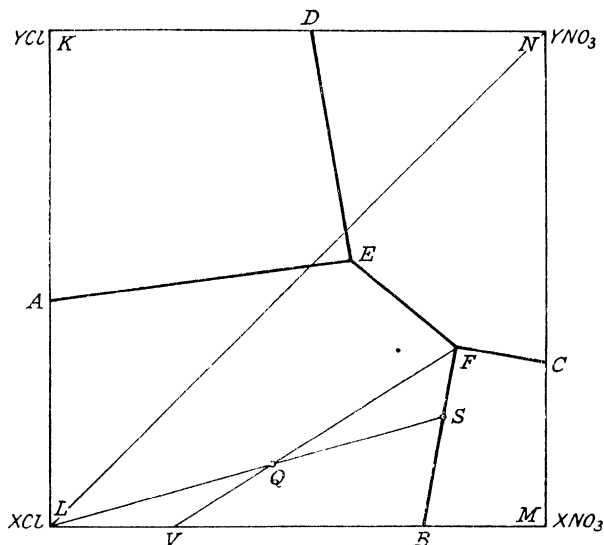


FIG. 30.

coincides with the square base of the pyramid. The new figure has also been rotated through  $45^\circ$  for convenience of plotting as will be seen later. Water is no longer represented at a point in the centre but has disappeared from the diagram. In Fig. 28 a change in the amount of water in a complex moves the point representing the complex. In Fig. 30, however, as the eye is imagined to be at the water apex, change in the amount of water, although it moves the point in space, does not alter its apparent position on the projection because the movement in space is in a straight line towards or away from the viewpoint. A point, therefore, on Fig. 30 represents the composition of a complex in terms of the salts it contains, but gives no information as to the amount of water present.

<sup>1</sup> "Über eine neue Darstellungsform der van't Hoff'schen Untersuchung über ozeanische Salzablägerungen," *Z. anorg. Chem.*, 1906, **51**, 132; 1907, **52**, 358, and 1907, **53**, 319.

The above means that in order to plot Jänecke's projection, the data must be expressed as the amount of each salt in mols in a fixed quantity, usually one mol, of salts, not in a fixed quantity of complex. In other words, water must be eliminated from the plotting

TABLE 23  
THE QUATERNARY SYSTEM.  $\text{XCl} \cdot \text{YNO}_3 \cdot \text{Water}$   
RECIPROCAL SALT PAIR

The data in Table 22 has been calculated to mols per mol of salts and is given below. Water is in mols per mol of salts and is the same for both sets of figures.

23A

Point.	Mols per Mol of Salts					Mol Ions per Mol of Salts.			
	XCl.	YCl.	XNO <sub>3</sub>	YNO <sub>3</sub>	Water	X	Y	Cl	NO <sub>3</sub>
K	—	1	—	—	2.28	0	1	1	0
L	1	—	—	—	1.44	1	0	1	0
M	—	—	1	—	0.785	1	0	0	1
N	—	—	—	1	1.27	0	1	0	1
A	0.543	0.457	—	—	1.15	0.543	0.457	1	0
B	0.247	—	0.753	—	0.835	1	0	0.247	0.753
C	—	—	0.667	0.333	0.725	0.667	0.333	0	1
D	—	0.470	—	0.530	1.15	0	1	0.470	0.530
E	0.400	—	0.600	0.400	0.800	0.400	0.400	0.400	0.600
F	0.181	—	0.819	0.181	0.710	0.637	0.363	0.181	0.819
H	0.550	—	0.320	0.130	2.05	0.870	0.120	0.550	0.450
O	0.550	—	0.320	0.130	1.06	"	"	"	"
P	0.550	—	0.320	0.130	0.42	"	"	"	"
T	0.550	—	0.320	0.130	0.25	"	"	"	"
Q	0.550	—	0.320	0.130	0.0	"	"	"	"

data. Table 23 has been thus calculated from the data in Table 22. A column for water has been included because it will be required later: these figures express the water as mols of water associated with one mol of salts at each point.

Any point on the diagram represents one mol of salts, mixed or pure according to its position, but with the amount of water unspecified. Since the amount of salt is fixed at one mol it is not possible to represent pure water on the figure because, however much water is added, there is always one mol of salts. Pure water can be considered as at infinity vertically above the projection.

In Chapter VIII methods of plotting points within a square were fully described. The figures in Table 23 may be used to plot the points for Fig. 30 in the same way, remembering that where three figures are given as for point E the point is plotted as being within the triangle of the three salts to which the figures apply.

The more usual method is to express the data in terms of radicals or ions, as given in Table 23A. This also has been referred to when dealing with the base of the pyramid. In this case the diagonals of the square are ignored and only two figures are required to fix any point within the square providing that one figure is of a basic radical, and the other of an acid radical. Table 23A actually gives four figures for every point, but in each case two are redundant.

An advantage of Jänecke's projection is that having plotted any point its composition can be read back from the diagram. In fact, any point chosen within the figure can be given a composition by measuring its position in the square. It is important to realize just what such a composition implies, and Figs. 30 and 24 should be closely compared so that the eye becomes trained to visualize a correct picture of the whole system, from Jänecke's projection. The relation of the four fields of Fig. 30 to the whole system must be clearly understood. Primarily they represent the four saturation surfaces of Fig. 24, but it is better to regard them as representing the four small inverted pyramids of Fig. 25. This is because the usual use of these diagrams is to obtain one of the four salts pure and in the solid state, and for this result the complex must be within the corresponding field which is one of these four small pyramids. Hence, when a point on Jänecke's projection is read in terms of the salts, it is assumed that the water content in the complex is the amount demanded by the system to bring the complex within one of these inverted pyramids.

**Jänecke's Projection for Evaporation of Water.** In order to illustrate the value of this type of projection as compared with the orthogonal or the pictorial pyramid, it is proposed to outline the same evaporation problem as was taken in Chapter IX.

On Fig. 30 the point  $Q$  is in the same relative position as it was on the base of Fig. 29 and, as the projection is from the water apex, the point  $Q$  represents all points on the water line including  $H$ .

As water is evaporated from the solution  $H$  there is no movement of the complex on the diagram. The problem, therefore, is to follow the movement of the solution and solid phases during the evaporation, the water being assumed in each case to be that which the equilibrium demands.

During evaporation from  $H$  to  $O$  (the letters  $H, O, P, T, Q$  refer to Fig. 29,  $Q$  being the point on Fig. 30) there is no separation of solid and so, from the point of view of Jänecke's projection, there is no change in composition of the salts in solution.

As the complex changes from  $O$  to  $P$  (Fig. 29)  $\text{XCl}$  is deposited as solid phase and the solution moves from  $Q$  towards  $S$  on a straight line drawn from  $\text{XCl}$  through  $Q$ . Thus, on this projection the composition of the salts in solution  $S$ , or in any intermediate solution between  $Q$  and  $S$ , is found accurately. The curve  $LOS$  (Fig. 29) must lie on a plane constructed from the edge  $W, \text{XCl}$ , because the only components removed from the solution  $O$  are water (by evaporation) and  $\text{XCl}$  (by crystallization). This plane must cut any other plane, in this case the base of the figure, in a straight line. Thus *paths of crystallization on Jänecke's projection are straight lines when a single salt is being deposited*.

The solution  $S$ , Fig. 30, is saturated with two salts  $\text{XCl}$  and  $\text{XNO}_3$ . On the removal of more water, these two salts will be deposited and the composition of the solution will move along the curve  $BF$  towards  $F$ , while at the same time the composition of the solid phase will move along the edge of the square from  $\text{XCl}$  towards  $V$ . When the solution reaches  $F$  the total solid phase is at  $V$ ,  $FQV$  being a straight line.

On further evaporation the composition of the solution remains constant at  $F$  while three salts are now deposited,  $\text{XCl}$ ,  $\text{XNO}_3$  and  $\text{YNO}_3$ , these being the salts with which the solution is saturated. Furthermore, these salts are deposited in the same proportion as they appear in the solution. Thus the composition of the total solid phase moves from  $V$  towards  $F$ , reaching  $Q$  when the complex is completely dried up.

To sum up: the composition of the solution moves from  $Q$  to  $S$  while pure  $\text{XCl}$  is deposited, from  $S$  to  $F$  while a mixture of  $\text{XCl}$  and  $\text{XNO}_3$  is deposited, and remains at  $F$  while the three salts are deposited. The amount of salts in solution relative to those

deposited is found at any stage by the usual ratio methods. For example, when the solution is at  $S$ ,  $SQ$  represents solid  $XCl$  and  $XCl.Q$  represents the salts in solution  $S$ . It must not be forgotten that so far the water content has been ignored.

**Advantages of Jänecke's Projection.** The advantages of this type of diagram over those of Figs. 24 and 28 are :

- (i) ease of plotting a point,
- (ii) there is only one scale for measurement,
- (iii) any point found can be read in terms of the salts,
- (iv) the saturation surfaces are not compressed into a small area,
- (v) the paths of crystallization are straight lines so that solution points are determined accurately.

It has to be admitted that water is ignored on Jänecke's projection and this might be considered a serious disadvantage. It is, however, considered better to introduce water in another way than to lose the advantages of this type of projection. As a matter of fact, most problems can be solved in outline on Jänecke's diagram without any need to know the amount of water until the final stage, and then by quite simple means the required water contents are determined. In other words, Jänecke's projection is sufficient where relative solubilities are more important than the absolute solubility of each salt.

**Jänecke's Projection plus Water.** Fig. 31 is a pictorial and isometric projection of a Jänecke's diagram in which the water content has been plotted vertically. The base of the figure is a square, undistorted but rotated into a suitable position. Jänecke's projection is plotted on this square from the data in Table 23. From the same table the water data are used to plot a new series of points, which are plotted vertically above their corresponding points on the base. When the necessary lines and curves have been drawn the resulting figure is a square prism with the four saturation surfaces forming its upper boundary.

The new diagram is really the pyramid of Fig. 24, but with its four edges vertical. It obeys the same rules as the pyramid, except that pure water cannot be represented, as it now lies at infinity and therefore water lines are vertical. Also these water lines are all drawn to the same scale which is an advantage over the pyramid. The composition of a complex, in terms of mols per mol of salts, is read on the base, and the mols of water per mol of salts are read upwards. When preparing the diagram any convenient scale may be used for water.

In Fig. 29 the point  $H$  was chosen to represent an unsaturated solution from which water was to be evaporated. In Fig. 31 the line  $HOPT'Q$  represents the path of evaporation of the complex and it is vertical. The measurement, using the water scale, of any part of that line gives directly the mols of water concerned in a particular operation. Thus the length  $HO$  represents the mols of water removed from a solution  $H$ , comprising one mol of salts and  $HQ$  mols of water, in order to obtain a solution of composition  $O$ . It therefore only remains to be able to plot the points  $O$ ,  $P$ ,  $T$  and  $Q$  accurately to be able to give a quantitative description of the evaporation of solution  $H$ .

The point  $Q$  is plotted as described for Jänecke's projection, Fig. 30. A vertical line is drawn from  $Q$ , and  $H$  is marked since the mols of water per mol of salts in the solution  $H$  is known. The position of  $O$ , where the solution is just saturated with  $XCl$ , is determined by drawing a line from  $XCl$  through  $Q$  to meet the curve  $BF$  at  $S$ . From  $S$  a vertical line is drawn to meet the curve  $B_1F_1$  at  $S_1$ . The line  $L_1S_1$  is drawn and, assuming the saturation surface is a plane, where this line cuts  $HQ$  is the point  $O$ .

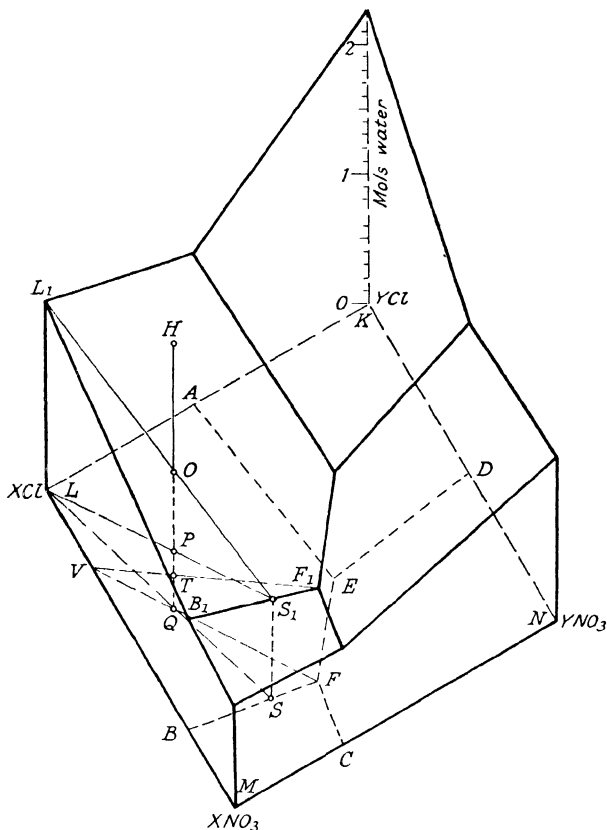


FIG. 31.

The point  $P$  is found by drawing the straight line  $LS_1$  to cut  $HQ$  at  $P$ .

The point  $T$  is found by drawing lines  $FQ$ , produced to  $V$ , and  $VF_1$  to cut the water line at  $T$ .

Thus Fig. 31 is a diagram which can be used in the same way as the pyramid, but with the added advantage that the complete composition of any solution or complex can be read directly from the diagram. For example:

$P$ reads	XCl.	$YNO_3$ .	$XNO_3$ .	Water.
$S$ „	0.55	0.13	0.32	0.427 in 1.427 mols complex $P$
	0.203	0.230	0.567	0.753 in 1.753 „ solution $S_1$

These figures are readily calculated to mols %.

	XCl.	$YNO_3$ .	$XNO_3$ .	Water.
$P =$	38.60	9.10	22.40	29.90
$S =$	11.57	13.13	32.40	42.90

The amount of water to be evaporated from solution  $H$  to give complex  $P$  may be found by measuring the distance  $HP$ , which is 1.623 units of the water scale. That is, 1.623 mols of water must be removed from a quantity of solution  $H$  which contains 1 mol of salts. The water in  $H$ , i.e.  $HQ$ , measures 2.05 mols. So 1 mol salts in  $H$  becomes  $1 + 2.05 = 3.05$  mols solution  $H$ .

$$\begin{aligned} 3.05 \text{ mols} - 1.623 \text{ mols water} &= 1.427 \text{ mols complex } P. \\ (1.427 \text{ mols complex } P &= 1 \text{ mol salts, } 0.427 \text{ mols water.}) \end{aligned}$$

When the complex is  $P$  it is a mixture of solid  $XCl$  and solution  $S_1$ . The proportions of solid to liquid are found by measuring the proportions of the line  $SQ$  and  $XCl.Q$ . By reading these distances on the scale of the base it will be found that

$$\begin{aligned} 7.97 \text{ mols } Q &= 3.47 \text{ mols } XCl, 4.5 \text{ mols } S \text{ (salts in solution } S_1) \\ 1 \text{ mol } Q &= 0.435 \text{ mols } XCl, 0.565 \text{ mols } S \\ 1 \text{ mol } Q &= 0.427 \text{ (} QP \text{) mols water} = 1.427 \text{ mols complex } P \\ 1 \text{ mol } S &= 0.753 \text{ (} SS_1 \text{) mols water} = 1.753 \text{ ,, solution } S_1 \\ \text{so} \quad 0.565 \text{ mols } S &= 1.753 \times 0.565 = 0.992 \text{ ,, ,, } S_1. \end{aligned}$$

That is, 1.427 mols complex  $P = 0.435$  mols solid  $XCl + 0.992$  mols solution.

**Jänecke's Projection plus Water (simplified).** Provided the principles of Fig. 31 are clearly understood, it is not always necessary to have the complete isometric figure. A simple plan and elevation of it makes it possible to draw the diagram on squared paper. The plan is simply Jänecke's projection and the elevation is a horizontal view of the curve or curves being used. Fig. 32 shows such a simplification. It is the same as Fig. 30 as regards the plan, except that it has been rotated for convenience to make the  $YCl.XCl$  line the base.

For the elevation the line  $YX$  is the base because on the  $Y$  side are  $YNO_3$  and  $YCl$ , while on the  $X$  side there are  $XNO_3$  and  $XCl$ . The projection of any point is easily marked on the elevation by projecting upwards vertically from the plan and measuring the water content (in mols) from the base line using any convenient scale. In the particular example which has thus far been considered, i.e. evaporation of water from solution  $H$ , it is only necessary to plot on the elevation that part of the diagram associated with the point  $H$ . ( $H$  is plotted on the elevation and  $Q$  is its position on the plan.) Thus the curve  $F_1S_1B_1$  has been drawn by projecting the points  $FSB$  along the vertical lines of the paper and plotting the mols of water for  $F$ ,  $S$  and  $B$  respectively. The mols of water for pure  $XCl$  are also plotted at  $L_1$  and a vertical line is drawn from  $Q_1$  through  $H$  to represent the water line. On the plan a line from  $XCl$  through  $Q$  gives  $S$ , which is projected on to the curve  $F_1B_1$  at  $S_1$ .

From  $S_1$  a line drawn to  $L_1$  cuts the water line at  $O$  and a similar line to  $X$  cuts the water line at  $P$ . Finally, a line from  $F_1$  to  $X$  (now representing the point  $V$  of the plan) cuts the water line at  $T$ . The diagram is thus complete for an evaporation problem, the points  $O$ ,  $P$ ,  $T$  and  $Q$  being interpreted as described for Fig. 31.

In using this simplified diagram the elevation may be drawn on any side of the square, but it is generally convenient to choose the side which gives the elevation of the required curve without undue foreshortening. In addition to the ease of plotting and reading, the method of representing water used in Fig. 32 has the advantage that two or more temperatures can be shown on one diagram.



FIG. 33a.

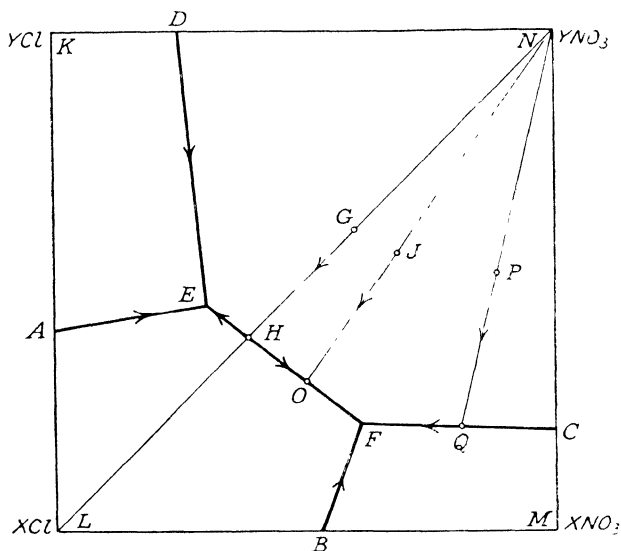
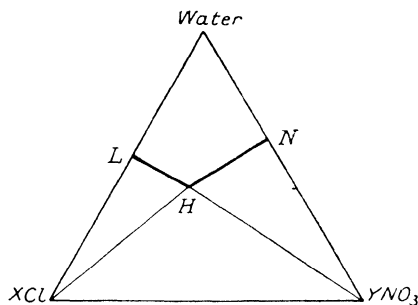


FIG. 33.

The four saturation surfaces can be divided into two pairs. The YCl and XNO<sub>3</sub> are the *unstable pair*, because the surfaces are separated by the length of the curve EF and these salts cannot exist in equilibrium with each other and a solution. The XCl and YNO<sub>3</sub> surfaces form the *stable pair* because they can both exist together in equilibrium in contact with a solution, the solution being at any point on the curve EF. If the solution is at H, then not only do the two salts XCl and YNO<sub>3</sub> form a stable pair, but they form with water a ternary system in spite of the absence of a common ion.

If the point G lies on the saturation surface it represents a solution just saturated as to YNO<sub>3</sub>. If water is evaporated isothermally the point representing the composition of



TABLE 24  
THE QUATERNARY SYSTEM.  $\text{XCl} \cdot \text{YNO}_3 \cdot \text{WATER}$   
RECIPROCAL SALT PAIR AT LOWER TEMPERATURE

For the same reciprocal salt pair as given in Tables 22 and 23 but the figures below are for a lower temperature.

Mols per Mol of Salts.					Mol Ions per Mol of Salts.			
Point	XCl.	YCl.	XNO <sub>3</sub>	YNO <sub>3</sub>	Y.	NO <sub>3</sub> .	Water.	Solid Phase.
K <sub>1</sub>	—	1	—	—	1	0	3.0	YCl
L <sub>1</sub>	1	—	—	—	0	0	1.9	XCl
M <sub>1</sub>	—	—	1	—	0	1	1.4	XNO <sub>3</sub>
N <sub>1</sub>	—	—	—	1	1	1	2.7	YNO <sub>3</sub>
A <sub>1</sub>	0.600	0.400	—	—	0.400	0	1.8	XCl + YCl
B <sub>1</sub>	0.470	—	0.530	—	0	0.530	1.33	XCl + XNO <sub>3</sub>
C <sub>1</sub>	—	—	0.800	0.200	0.200	1	1.26	XNO <sub>3</sub> + YNO <sub>3</sub>
D <sub>1</sub>	—	0.750	—	0.250	1	0.250	2.39	YCl + YNO <sub>3</sub>
E <sub>1</sub>	0.550	0.150	—	0.300	0.450	0.300	1.565	XCl + YNO <sub>3</sub> + YCl
F <sub>1</sub>	0.390	—	0.400	0.210	0.210	0.610	1.20	XCl + YNO <sub>3</sub> + XNO <sub>3</sub>

the solution moves in a straight line from  $\text{YNO}_3$  through  $G$  to meet the curve  $EF$  at  $H$ . That is, the diagonal is the path of crystallization. When the solution is at  $H$  further evaporation causes both  $\text{YNO}_3$  and  $\text{XCl}$  to be deposited in the same proportion as they are present in the solution, so that the composition of  $H$  now remains unchanged, and if sufficient water is removed the solution finally dries up at composition  $H$ . (See Chapter VI on ternary systems.)

A point representing a saturated solution on any other part of the  $\text{YNO}_3$  surface and not falling on the diagonal  $\text{YNO}_3 \cdot \text{XCl}$  would, on the removal of water, deposit  $\text{YNO}_3$  and the solution point would move towards the curve  $EF$  or either of the curves  $FC$  or  $ED$ , according to the position chosen. When the point reached the curve the solution would be saturated with two salts,  $\text{YNO}_3$  and one of the other three. The second salt would be  $\text{YCl}$  if the path of crystallization met the curve  $ED$ ,  $\text{XCl}$  for the curve  $EF$  and  $\text{XNO}_3$  for the curve  $FC$ .

When the solution point reached the curve, the removal of more water would cause two salts to be deposited and the point would move along the curve *away from* a point representing the composition of the *solid phase being deposited*. For example, the point  $P$  moves along the path of crystallization drawn from  $\text{YNO}_3$ , and when the point meets the curve at  $Q$  the solution is saturated with  $\text{YNO}_3$  and  $\text{XNO}_3$ . If more water is removed  $\text{YNO}_3$  and  $\text{XNO}_3$  are deposited, and the composition of the mixture is represented by a point near  $C$  (actually  $C$  if  $FC$  is a straight line). The solution point must therefore move away from  $C$ , that is, towards  $F$ . In the same way a solution point moving along the line drawn from  $\text{YNO}_3$  through the point  $J$  represents a solution which when at  $O$  is saturated with both  $\text{YNO}_3$  and  $\text{XCl}$ . On the further isothermal evaporation of water both  $\text{YNO}_3$  and  $\text{XCl}$  will be deposited, and the solution point will move away from the point representing the composition of the mixture which is being deposited. This point must be  $H$ , because the composition of the mixture lies on  $EF$ , assuming  $EF$  to be a straight line and the mixture contains only  $\text{YNO}_3$  and  $\text{XCl}$ . The point  $O$  therefore moves towards  $F$  in the same way as did the point  $Q$ .



There are four saturation surfaces similar to those on Fig. 33. One pair of these surfaces,  $\text{YNO}_3$  and  $\text{XCl}$ , form the stable pair and the other pair  $\text{YCl}$  and  $\text{XNO}_3$  form the unstable pair, as was the case in Fig. 33. In contrast, however, with Fig. 33 neither diagonal divides the Fig. 34 isotherm into two similar systems because the point  $E$  has moved over to the other side of the  $\text{XCl}.\text{YNO}_3$  diagonal and is within the system  $\text{XCl}.\text{YNO}_3.\text{XNO}_3.\text{water}$ , that is, it is within the same system as is the point  $F$ . Again, neither diagonal can be formed into a ternary system, the whole internal system being quaternary. The point  $E$  is *incongruent*.

Phase reactions in the  $\text{XNO}_3$  field in Fig. 34 are exactly the same as for Fig. 33; in the three remaining fields there are certain differences.

In either of the two fields forming the stable pair, that is  $\text{XCl}$  and  $\text{YNO}_3$ , there are three types of phase reactions. Taking the diagonal  $\text{XCl}.\text{YNO}_3$ , two of these types occur when the point representing the complex falls on that side of the diagonal on which lies the curve dividing the stable pair ( $EF$ ). The first case is when the path of crystallization meets one of the three curves  $EF$ ,  $FB$  or  $FC$ . For example, the point  $G$  where the path of crystallization meets the curve  $EF$ , or  $G_1$  where the path meets the curve  $FB$ . Taking  $G$  to represent a solution saturated with  $\text{XCl}$ , then on the removal of water the solution point moves to  $H$  where the solution is saturated with  $\text{XCl}$  and  $\text{YNO}_3$ . On removing more water the solution point moves towards  $F$  as both  $\text{YNO}_3$  and  $\text{XCl}$  are being deposited. The composition of the mixture passing into the solid phase during this period is represented by  $S$  on the diagonal. When the solution was at  $H$  the solid phase was  $\text{XCl}$ , and by the time the solution point has moved from  $H$  to  $F$  the solid phase has moved from  $\text{XCl}$  towards  $S$  to the point  $J$ . From the point  $F$  the further removal of water deposits all three salts, the mixture deposited having the composition  $F$ . Nor does the solution composition change, but remains at  $F$  until dried up.

The phase reactions of  $G_1$  are similar, except that the mixture of two salts is  $\text{XCl}$  and  $\text{XNO}_3$  of composition  $B$ . Points similar to  $G$  and  $G_1$  could have been chosen in the  $\text{YNO}_3$  field.

The second type of phase reaction in either of the fields forming the stable pair is when the position of the complex on the saturation surface, though still on the same side of the diagonal  $\text{XCl}.\text{YNO}_3$ , is such that the path of crystallization meets the curve  $ED$  or  $EA$ . The point  $T$  may be taken as an example, where the line from  $\text{YNO}_3$  through  $T$  meets the curve  $ED$  at  $O$ . Removal of water beyond that stage causes two salts,  $\text{YNO}_3$  and  $\text{YCl}$ , to be deposited while the solution point moves from  $O$  to  $E$  and when the solution is at  $E$  the solid phase is at  $W$ . The solution at  $E$  is now saturated with three salts,  $\text{XCl}$ ,  $\text{YNO}_3$  and  $\text{YCl}$ . The removal of water causes  $\text{XCl}$  and  $\text{YNO}_3$  to be deposited and  $\text{YCl}$  to be dissolved, the composition of the solution being unchanged. (This is explained later with Fig. 34a.) The solid phase moves from  $W$  towards  $E$ , arriving at  $V$  on the diagonal when all the  $\text{YCl}$  is dissolved. On still further removal of water the composition of the solution moves from  $E$  towards  $F$ , that is, away from  $S$ , which represents the mixture being deposited. The solid phase now moves from  $V$  towards  $U$ , arriving at  $U$  when  $F$  is the composition of the solution. Then, as the solution dries up at composition  $F$ , the solid phase moves from  $U$  to  $T$ .

The third type of phase reaction within the  $\text{XCl}$  or  $\text{YNO}_3$  field is when the complex falls within the system  $\text{XCl}.\text{YNO}_3.\text{YCl}.\text{water}$ , that is, on the other side of the diagonal, and the point  $Q$  can be used as such an example. With water removal the solution point moves from  $Q$  to  $Z$  and  $\text{XCl}$  is the solid phase. The solution point then moves along the

curve from  $Z$  to  $E$  and  $XCl$  and  $YCl$  are deposited, the composition of the deposit being  $A$ , but the composition of the total solid phase moving from  $XCl$  to  $I$ . Further isothermal evaporation causes  $XCl$  and  $YNO_3$  to be deposited and  $YCl$  to be dissolved, but the composition of solution  $E$  remains unaltered. The composition of the solid phase moves from  $I$  towards  $Q$ , and arrives at  $Q$  when the solution has dried up at composition  $E$ . The point  $E$  is therefore a drying-up point, but it is *incongruent*, and so not a final drying-up point. It is a drying-up point only if the complex lies within the system which has for its components the three salts with which it is saturated.

The point  $E$  is said to be incongruently saturated because, although it is saturated with  $XCl$ ,  $YNO_3$  and  $YCl$ , its composition cannot be expressed in positive terms of those three salts. An incongruently saturated, quaternary invariant point such as  $E$  is not a drying-up point at all if the solid phase is removed as the evaporation proceeds. In that case, when the solution reaches composition  $E$ , as the solids have been removed, there is no solid  $YCl$  to be dissolved and the composition of the solution does not even pause at  $E$  but moves straight on to  $F$ , that is,  $F$  is the only true drying-up point in the whole system.

The arrow-heads on the paths of crystallization show how the composition of the solutions move from the complexes to the curves, and the arrow-heads on the curves, themselves paths of crystallization, show how the compositions move towards  $F$ .

Finally, the  $YCl$  field may be regarded as divided by the diagonal  $XCl.YNO_3$ , and complexes on either side of this diagonal behave similarly to the second and third types already described for the stable pair fields.

The isotherms represented on Figs. 33 and 34 are both common types and will serve as examples of all cases where no double salts or hydrated solid phases are formed. It is quite common for the isotherm to take one form such as Fig. 33 at one temperature and another form as Fig. 34 at another temperature. It is also possible through a temperature range for the changes in the form of the isotherm to be such that the stable pair at one temperature becomes the unstable pair at another temperature. This could only come about by the curve  $EF$  becoming shorter and shorter until  $E$  and  $F$  were at one point and then for  $E$  and  $F$  to diverge again, but in a direction which pulls the fields of the former stable pair apart so that they now become the unstable pair. This shows that still another form of isotherm is possible, that is, when  $E$  and  $F$  are at one point which represents a solution saturated with all four salts at a certain definite temperature.

On page 103 it was stated that the composition of the *incongruently saturated invariant solution*, represented by the point  $E$  on Fig. 34, is not changed by the removal of water if the temperature is not allowed to alter. According to the phase rule the composition cannot change so long as the three solid phases,  $XCl$ ,  $YCl$  and  $YNO_3$  are in contact with the solution, making four phases in all. (See Chapter XIII.) The system is quaternary and is condensed, so the formula becomes

$$\begin{aligned} C + 1 &= P + F \\ 4 + 1 &= 4 + 1 \end{aligned}$$

The one degree of freedom has been used up by choosing the temperature of the isotherm, and so the composition of the solution, represented by the point  $E$ , is fixed by nature.

Although the composition of solution  $E$  does not change, the removal of water causes two solid phases,  $XCl$  and  $YNO_3$ , to be deposited and the solid phase  $YCl$  to dissolve. The phase rule gives no direct indication of this; it merely states that three solid phases must be present. The phase diagram shows what these three solid phases are and also shows

that one of the solid phases, and which one, will dissolve as the others are deposited. Fig. 34a demonstrates how it is possible for  $\text{XCl}$  and  $\text{YNO}_3$  to be deposited from solution  $E$ , for  $\text{YCl}$  to dissolve when water is removed, and for the composition of the solution to be unchanged. This figure is a reproduction of Fig. 34 with the appropriate lines.

On Fig. 34*a* the line from  $\text{YNO}_3$  to a point  $a$  passes through  $E$ . The point  $a$  may be chosen within limits and the distance from  $E$  to  $a$  gives the proportion of  $\text{YNO}_3$  deposited from solution  $E$ . The line from  $\text{XCl}$  and through the point  $b$  passes through  $a$  and the distance from  $a$  to  $b$  gives the proportion of  $\text{XCl}$  deposited from the composition represented by point  $a$ . The line from  $\text{YCl}$  through the point  $b$  passes through  $E$  and the distance  $b$  to  $E$  gives the proportion of  $\text{YCl}$  added to the composition, represented by the point  $b$ , in order to give composition  $E$ .

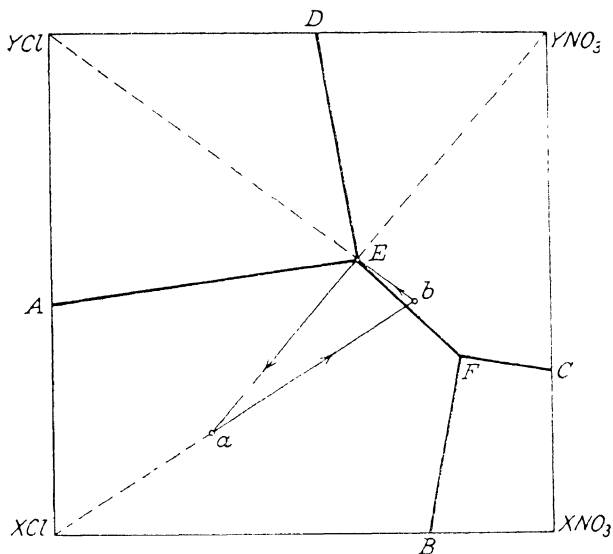


FIG. 34a.

Water could have been shown on an elevation, but it is not necessary ; if the composition of the salt mixture in the solution is unchanged and the temperature is unchanged, then the composition of the solution is unchanged so long as the three solid phases are present and the system is at equilibrium. The following calculation is a quantitative proof that solution *E* can remain unchanged in composition.

If the distances are measured parallel to the base of the square which represents 1 mol and is considered as divided into 100 parts

0.300 mol of $\text{YNO}_3$ is removed from 0.7 mol of salts in solution $E$		
$\therefore$ 0.428	"	1.0
"	"	"
"	"	"

This leaves  $1.0 - 0.428 = 0.572$  mol of mixture of composition  $a$

0.400 mol of XCl is removed from 0.700 mol of salts in mixture *a*  
 $\therefore$  0.327                      "                      "                      0.572                      "                      "                      "

This leaves  $0.572 - 0.327 = 0.246$  mol of salts in mixture *b*.

0.100 mol of YCl is added to 0.600 mol of salts in mixture *b*  
 $\therefore$  0.041        „        „        „        0.246        „        „        „

To summarize :

	X.	Y.	Cl	NO <sub>3</sub> .
1.000 mol of solution <i>E</i>	= 0.458	0.542	0.400	0.600
0.428 mol YNO <sub>3</sub> deposited	=	0.428		0.428
0.572 mol salts in solution	= 0.458	0.114	0.400	0.172
0.327 mol XCl deposited	= 0.327		0.327	
0.246 mol salts in solution	= 0.131	0.114	0.073	0.172
0.041 mol YCl dissolved	=	0.041	0.041	
0.286 mol salts in solution	= 0.131	0.155	0.114	0.172
1.000 mol salts in solution	= 0.458	0.542	0.400	0.600

and the first solution is still *E*.

**Heating and Cooling.** The two isotherms represented in Figs. 33 and 34 have been plotted on one diagram as Fig. 35 for the purpose of studying the principles of heating and cooling. An example in the XNO<sub>3</sub> field, say the point *G* (Fig. 35), may be taken to represent a solution saturated with XNO<sub>3</sub> and XCl but containing some YNO<sub>3</sub> and at the higher temperature. This solution is now cooled to the lower temperature when the point *G* falls within the XNO<sub>3</sub> field on the plan. Draw a line from XNO<sub>3</sub> through *G* to meet the curve *F*<sub>1</sub>*B*<sub>1</sub> on the plan when the point *H* represents the composition of the solution, but only if the amount of water is such that *H* falls on the curve *F*<sub>1</sub>*B*<sub>1</sub> at the given lower temperature. If the amount of water is too small the case is equivalent to water having been evaporated and the solution point will have moved from *H* towards *F*<sub>1</sub>. If the amount of water is too great the solution point will not have reached *H* but will be on the XNO<sub>3</sub> saturation surface somewhere on the line *GH*.

Mark the point *G* on the elevation of the curve *FB* and draw a line from NO<sub>3</sub> (representing XNO<sub>3</sub>) through *G* on the elevation. It will be seen that this line does not meet the curve *F*<sub>1</sub>*B*<sub>1</sub> on the elevation. Now draw a line on the elevation from *H* to *C*<sub>1</sub>, that is, on the saturation surface, and where this line cuts the line from NO<sub>3</sub> through *G* is the point *I*. Project the point *I* on to the plan and mark it on the line *GH* at *I* on the plan. Then, if *G* represents a solution at the higher temperature and if this solution is cooled to the lower temperature, the solid phase will be pure XNO<sub>3</sub> and the solution will be represented by *I*. The amount of water in solution *I* is read from the elevation, while the composition of solution *I* and the proportion of solution to solid is read from the plan. The proportion can, of course, be read from the elevation, but the plan is more convenient.

Thus :

Solution *G* before cooling (1 mol of salts) has the composition

XCl.	YNO <sub>3</sub> .	XNO <sub>3</sub> .	Water.
0.235	0.065	0.700	0.80 mol

After cooling :

0.365 mol *G* = 0.235 mol solution *I* + 0.13 mol XNO<sub>3</sub>  
 (XNO<sub>3</sub> to *I*)    (XNO<sub>3</sub> to *G*)                    (*I* to *G*)  
 i.e.        1 mol *G* = 0.644 mol solution *I* + 0.356 mol XNO<sub>3</sub>

The composition of solution *I* (1 mol salts) is

	XCl.	YNO <sub>3</sub> .	XNO <sub>3</sub> .	Water.
Thus 0.644 mol =	0.365	0.100	0.535	1.26 mol
	0.235	0.065	0.344	0.80 mol

Subtract 0.644 mol of solution *I* from 1 mol solution *G* and the mols XNO<sub>3</sub> deposited will be found to agree with the figure given above.

	XCl.	YNO <sub>3</sub> .	XNO <sub>3</sub> .	Water.
<i>G</i> =	0.235	0.065	0.700	0.80 mol complex
<i>I</i> =	0.235	0.065	0.344	0.80 mol liquid phase
—	—	—	0.356	— mol solid phase

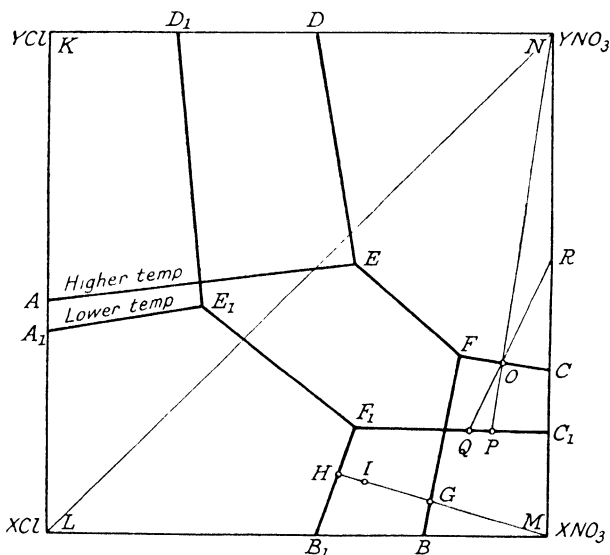
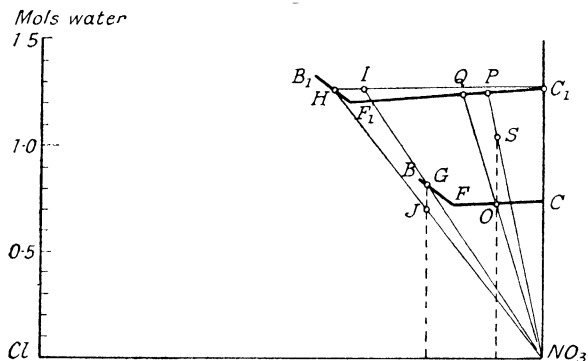


FIG. 35.

A greater yield of solid  $\text{XNO}_3$  would have been obtained if the point  $I$  had been very near to  $H$ . On the elevation draw a line from  $H$  to  $\text{NO}_3$ , and where this line cuts the  $G$  water line (the vertical through  $G$ ) at the point  $J$  gives the mols of water that the original complex  $G$  should contain in order to obtain the maximum yield of solid  $\text{XNO}_3$ .  $G$  would not then be a clear solution at the higher temperature. The amount of water to be removed from a quantity of solution containing 1 mol of salts is found by measuring the distance  $GJ$  on the elevation. Had that amount of water been removed from solution  $G$  before cooling,  $G$  would have become a mixture of a solution on the curve  $FB$ , somewhere between  $G$  and  $F$ , and a solid made up of  $\text{XNO}_3$  with some  $\text{XCl}$ . On cooling this mixture and allowing it to reach equilibrium, the solid would be  $\text{XNO}_3$  and the solution would be represented by  $H$ .

As a different type of reaction take the point  $O$  on the curve  $FC$  to represent a solution at the higher temperature, saturated with  $\text{XNO}_3$  and  $\text{YNO}_3$ . On cooling the solution to the lower temperature the point  $O$  is within the  $\text{YNO}_3$  field on the plan. Draw a line from  $\text{YNO}_3$  through  $O$  to meet the curve  $F_1C_1$  at  $P$  and draw a similar line from  $\text{NO}_3$  (representing  $\text{YNO}_3$ ) through  $O$  on the elevation to meet the curve  $F_1C_1$  on the elevation. It will be noticed that this line does not meet the curve at the point  $P$  which was projected from the plan, but at  $Q$ , and if another elevation were drawn with  $Y$  and  $X$  as the base it would be seen that the line from  $\text{NO}_3$  through  $O$  did not meet the curve  $F_1C_1$  on the elevation at all but passed under it. It is, however, not necessary to draw another elevation. In order to fix a point in space three axes are needed; the diagram provides two of them and the third is provided by the well-known rule that the complex lies on a straight line drawn from the solid phase to the solution. The point  $\text{NO}_3$  on the elevation represents any mixture of  $\text{XNO}_3$  and  $\text{YNO}_3$  including, of course, the pure salts. If the line on the elevation drawn from  $\text{NO}_3$  through  $O$  is considered as drawn from some point on the side of the square representing a mixture of  $\text{XNO}_3$  and  $\text{YNO}_3$ , there must be a point  $Q$  on the curve  $F_1C_1$  representing a solution in phase with that solid and a straight line drawn from the point representing that solution to the point representing the mixed solid in phase with it must pass through  $O$ . If, therefore, a rod of adjustable length were hinged freely in space at  $O$ , one end of the rod could be moved along the edge of the plan  $\text{YNO}_3.\text{XNO}_3$  until the other end met the curve  $F_1C_1$  at the point  $Q$ . Actually all that is necessary is to draw the line  $\text{NO}_3.OQ$  on the elevation, project  $Q$  on to the plan and draw the line  $QOR$  on the plan. Then, on cooling solution  $O$  from the higher temperature to the lower temperature,  $Q$  represents the solution and  $R$  the solid phase.

Had the solution point been at  $P$  the solid phase would have been  $\text{YNO}_3$ , but, as there is too little water, the solution point has moved from  $P$  to  $Q$ . Adding water will move the solution point from  $Q$  towards  $P$  and the solid phase from  $R$  towards  $\text{YNO}_3$ . The amount of water to be added to the quantity of solution containing 1 mol of salts is indicated by the distance  $OS$  on the water line of the elevation (the vertical line) through  $O$ . The water could conveniently be added before the cooling.

Heating a solution or mixture of solution and solid is similar to cooling except that the reactions take place in the reverse order.

Similar examples could be taken for solution on the curves  $DE$  or  $AE$  with similar results. An example on the curve  $EF$ , but with a different salt pair, will be studied in the next chapter. The points  $G$  and  $O$  representing the hot solution need not have been on the curves. Had they been lying on the saturation surfaces, that is saturated with one salt only, it would have made no difference to the principles involved. The above examples



have made it clear that when studying phase reaction by means of Jänecke's projections of the isotherms, the complex does not change its position during heating or cooling nor during the addition or removal of water. It is only the points representing the solution and the solid phase respectively that can move and the three points representing solution, complex and solid phase always lie on one straight line.

# CHAPTER XI

## PRACTICAL EXAMPLES USING JÄNECKE'S PROJECTION

**Preparation of Potassium Nitrate from Sodium Nitrate and Potassium Chloride.** The operations of heating and cooling, evaporating and diluting, adding and removing salts are all taken together in the process of making potassium nitrate from sodium nitrate and potassium chloride. The diagram required is shown in Fig. 36, which

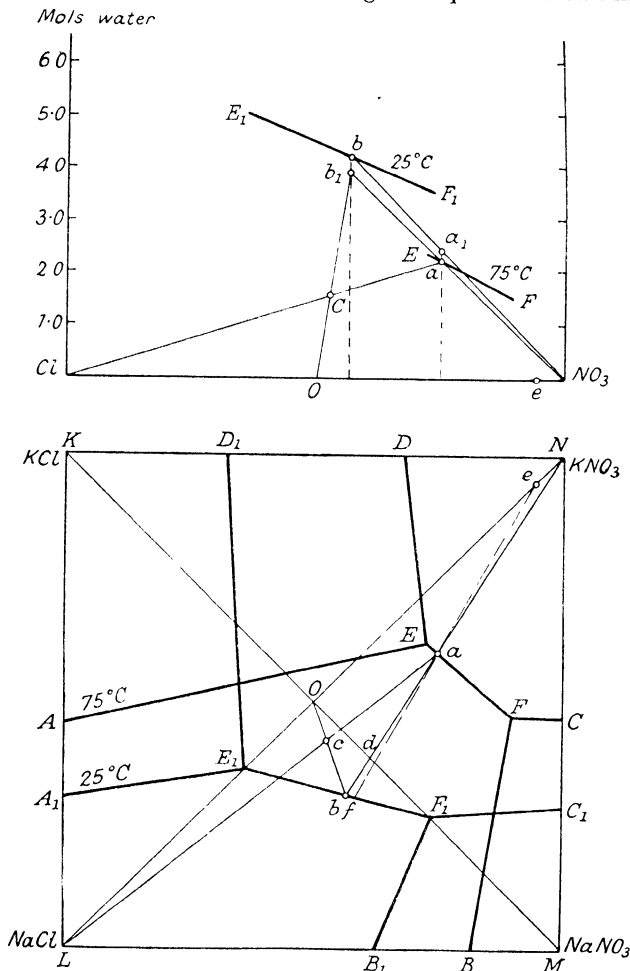


FIG. 36.

has been plotted from the data given in Table 25 and shows two isotherms, one at 25° C. and one at 75° C. for the system :



TABLE 25  
THE QUATERNARY SYSTEM,  $\text{NaNO}_3$ . $\text{KCl}$ .WATER, FORMING THE  
RECIPROCAL PAIR  $\text{NaNO}_3 + \text{KCl} \rightleftharpoons \text{KNO}_3 + \text{NaCl}$   
Mol Ions per Mol of Salts

Point.	25° C.			Point.	75° C.			Solid Phase.
	K.	NO <sub>3</sub> .	Water.		K.	NO <sub>3</sub> .	Water.	
$K_1$	1	0	11.51	$K$	1	0	8.33	KCl
$L_1$	0	0	9.01	$L$	0	0	8.53	NaCl
$M_1$	0	1	5.14	$M$	0	1	3.33	$\text{NaNO}_3$
$N_1$	1	1	14.65	$N$	1	1	3.67	$\text{KNO}_3$
$A_1$	0.303	0	7.63	$A$	0.45	0	6.41	NaCl + KCl
$B_1$	0	0.624	5.08	$B$	0	0.821	3.31	NaCl + $\text{NaNO}_3$
$C_1$	0.278	1	3.38	$C$	0.462	1	1.50	$\text{NaNO}_3 + \text{KNO}_3$
$D_1$	1	0.325	8.0	$D$	1	0.675	3.41	KCl + $\text{KNO}_3$
$E_1$	0.36	0.36	5.01	$E$	0.622	0.727	2.34	NaCl + $\text{KNO}_3$ + KCl
$F_1$	0.26	0.74	3.54	$F$	0.465	0.920	1.49	NaCl + $\text{KNO}_3$ + $\text{NaNO}_3$

Data at 25° C. from W. Reinders, *Z. anorg. Chem.*, 1915.

Data at 75° C. from E. Cornec and H. Krombach, *Caliche*, Sept. 1928.

The two isotherms are similar to those studied using  $X$  and  $Y$  for the positive ions, but it will be noticed that the amounts of water per mol of salts are in all cases much greater. This makes no difference to the principle nor to the general form of the diagram as a convenient scale may always be chosen for water.

At 75° C. the curve  $EF$  divides the fields of the stable pair of salts,  $\text{KNO}_3$  and NaCl, and solution  $F$  is congruently saturated while solution  $E$  is incongruently saturated.

At 25° C. the curve  $E_1F_1$  also separates the same stable pair, and the points  $E_1$  and  $F_1$  both represent solutions which are congruently saturated. Solution  $F_1$  is congruently saturated in the system NaCl. $\text{KNO}_3$ . $\text{NaNO}_3$ .water, but in addition to being represented in terms of the three salts mentioned it may be represented in terms of KCl and  $\text{NaNO}_3$ , because it falls on the diagonal between those two salts. The point  $F_1$  is therefore a ternary invariant point in the system KCl. $\text{NaNO}_3$ .water at 25° C.

The point  $E_1$  represents a solution saturated with NaCl. $\text{KNO}_3$  and KCl, and may be represented in terms of NaCl,  $\text{KNO}_3$  and no KCl.  $E_1$  is a ternary invariant point in the system NaCl. $\text{KNO}_3$ .water at 25° C.  $E_1$  and  $F_1$  are therefore both final drying-up points, but if the solution point is anywhere on the curve  $E_1F_1$  except at the point  $E_1$  on the diagonal, the solution point will move towards  $F_1$  and dry up at  $F_1$  on the removal of sufficient water.

It is now proposed to take as an example the production of potassium nitrate from a mixture of potassium chloride and sodium nitrate by double decomposition. The potassium nitrate will be obtained by cooling a suitable solution from 75° C. to 25° C. and removing the potassium nitrate crystals from the mother liquor. The raw material is a mixture of potassium chloride and sodium nitrate and these would conveniently be added

in equimolecular proportions represented by the centre of the square, point  $O$ . The mixture may also be considered as equimolecular proportions of sodium chloride and potassium nitrate.

The composition of the hot solution may conveniently be a point on the curve  $EF$  saturated with  $\text{KNO}_3$  and  $\text{NaCl}$ . Inspection shows that the greatest yield of  $\text{KNO}_3$  will be obtained (for the temperatures chosen) if the composition of the hot solution is near  $E$ . Let the point  $a$  be chosen to represent the composition of the hot solution; then  $b$  on the line  $\text{KNO}_3.a$  produced will be the composition of the cold solution. Solution  $b$ , after separating the  $\text{KNO}_3$  crystals, will be heated and the correct quantity of mixture  $O$  added to give a complex at  $c$ , and the temperature will be maintained at  $75^\circ\text{C}$ . until equilibrium is attained. The solid phase will then be  $\text{NaCl}$ , which is removed, and the composition of the solution will be at point  $a$  again. The process is cyclic: hot solution  $a$  is cooled, giving solid  $\text{KNO}_3$  and solution  $b$ ; solution  $b$  plus mixture  $O$  gives complex  $c$ , which when heated yields solid  $\text{NaCl}$  and solution  $a$ .

To start the process solution  $a$  or  $b$  must first be prepared. Solution  $b$  could be obtained by adding the correct amount of water to a mixture of  $\text{KCl}$  and  $\text{NaNO}_3$ , represented by the point  $d$  and cooling to  $25^\circ\text{C}$ . This would give solution  $b$  and a small yield of  $\text{KNO}_3$ .

Having traced out the cycle in what appears to be the best position on the plan projection, it is necessary to consider the amounts of water required in the various solutions.

Solution  $a$  is projected on the curve  $EF$  on the elevation, a line is drawn from  $a$  to  $Cl$  (representing  $\text{NaCl}$ ) and the point  $c$  is projected on this line. Solution  $b$  is projected on the curve  $E_1F_1$  and a line is drawn from this point to  $NO_3$  (representing  $\text{KNO}_3$ ). It will be seen that the line  $NO_3.b$  does not pass through the point  $a$ , but passes above it at  $a_1$ ; thus it is clear that in this case water must be added to solution  $a$  to move it into the all-liquid field at  $75^\circ\text{C}$ ., so that it will be in the  $\text{KNO}_3$  field during most of the cooling period and only reach the curve  $E_1F_1$  at the point  $b$  at the final temperature. The amount of water to be added for 1 mol of salts in solution  $a$  is given by the vertical distance between  $a$  and  $a_1$ .

After cooling, solution  $b$  contains the added water, and this is removed by concentrating the whole or a part of this liquor so that the solution is represented by the point  $b_1$ . The amount of water to be removed from 1 mol of salts in solution  $b$  is given by the vertical distance between  $b$  and  $b_1$ . The point  $b_1$  may be found by drawing a line from  $NO_3$  (representing  $\text{KNO}_3$ ) through  $a$  and producing to meet the water line drawn vertically from  $b$ . The removal of water from  $b$  is represented by a vertical line only, because when solution  $b$  is heated it becomes unsaturated and, on the  $75^\circ\text{C}$ . isotherm, is in the field of all liquid.

A line drawn from  $b_1$  to the point  $O$  on the elevation passes through the point  $c$ , and the original complex is again formed by mixing solution  $b_1$  and mixture  $O$  in the proportions obtained by measuring the line  $bcO$  on the plan.

The cycle of operations and reactions is summarized as follows:

- (1) Complex  $c$  at  $75^\circ\text{C}$ . yields solution  $a$  and solid  $\text{NaCl}$ .
- (2) Solution  $a$  with water added yields solution  $a_1$ , which is unsaturated at  $75^\circ\text{C}$ .
- (3) Solution  $a_1$  when cooled to  $25^\circ\text{C}$ . yields solution  $b$  and solid  $\text{KNO}_3$ .
- (4) Solution  $b$  when heated and water removed yields solution  $b_1$ , which is unsaturated when hot.
- (5) Solution  $b_1$  plus mixture  $O$  yields the original complex  $c$ .

The elevation on Fig. 36 is given on a larger scale as Fig. 36a, and it is now proposed to study the procedure and reactions in more detail. Starting from complex  $c$ , this mixture is agitated at  $75^\circ\text{C}$ . until it has reached equilibrium. In practice, the agitation might be

continued until samples of the clear liquor showed no further change in specific gravity at 75°C. The solid salt and the solution are then separated at 75°C. and solution *a* is

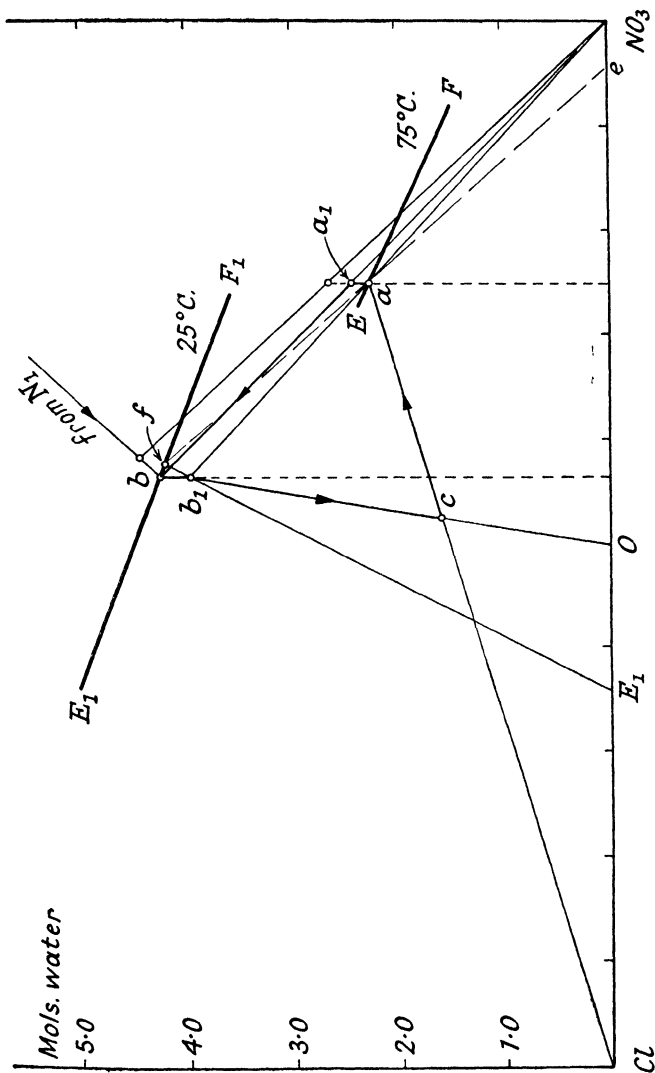


FIG. 36a.

diluted to give solution  $a_1$ , which is then allowed to cool to 25°C. to obtain solid potassium nitrate and solution  $b$ .

Solution  $a$  is on the curve  $EF$  at  $75^{\circ}\text{C}$ ., that is, the solution is saturated with  $\text{NaCl}$  and  $\text{KNO}_3$ , and in this case such a solution deposits both salts during cooling. Lines drawn from  $a$  and from  $b$  to both  $\text{Cl}$  and  $\text{NO}_3$  would form two triangles with  $a$  and  $b$  at the apices. Taking  $\text{Cl}.\text{NO}_3$  on the elevation as the base, the triangle which has its apex at  $a$  lies entirely inside the triangle which has its apex at  $b$ . Cooling solution  $a$ , therefore, will result in the solution remaining saturated with both  $\text{NaCl}$  and  $\text{KNO}_3$ , so that both salts will be deposited in the solid phase. These two salts  $\text{NaCl}$  and  $\text{KNO}_3$  behave in a similar way to  $\text{NaNO}_3$  and  $\text{KNO}_3$ . (See Fig. 17.)

If the solution represented by the point  $a$  on the elevation was cooled to  $25^{\circ}\text{C}$ . the solution would not be at  $b$  but at a point on the curve  $E_1F_1$  representing the solution obtained if water was removed from solution  $b$  at  $25^{\circ}\text{C}$ . The point  $F_1$  is the drying-up point of the system  $\text{NaCl}.\text{NaNO}_3.\text{KNO}_3$  at  $25^{\circ}\text{C}$ ., so if water were removed isothermally from solution  $b$ , the composition of the solution would move from  $b$  towards  $F_1$  on the plan. The composition of the solid phase, deposited during the evaporation, would be a mixture of  $\text{NaCl}$  and  $\text{KNO}_3$  represented on the diagonal by the point  $E_1$  (assuming  $E_1F_1$  is a straight line).

If the amount of water removed was equal to the amount which should have been added to solution  $a$  the composition of the solution would move from  $b$  to  $b_1$  on the elevation. The solid phase is on the base of the elevation at a point projected vertically from  $E_1$ . A line drawn from this point on the base of the elevation through  $b_1$  (which is the complex) cuts the curve  $E_1F_1$  at  $f$ , which represents the composition of the solution at  $25^{\circ}\text{C}$ . if no water was added to solution  $a$ . A line drawn on the elevation from  $f$  through  $a$  and produced, meets the base of the elevation at  $e$ , which represents the composition of the solid phase if solution  $a$  were cooled to  $25^{\circ}\text{C}$ . If a line is drawn on the plan from  $e$  through  $a$  and produced it cuts the curve  $E_1F_1$  at  $f$ , which is a projection of  $f$  on the elevation. (See Fig. 36a.)

It has now been shown that the solution represented by the point  $a$  must be diluted with water to move it vertically out of the field of  $\text{KNO}_3 + \text{NaCl}$  into the field of  $\text{KNO}_3$ . (See Figs. 25 and 26 for the systems  $\text{XNO}_3 + \text{YCl} = \text{XCl} + \text{YNO}_3$ .) If too much water is added to solution  $a$  at  $75^{\circ}\text{C}$ . the point representing the new solution would be moved still higher into the field of all liquid, with the result that on cooling to  $25^{\circ}\text{C}$ . the solution would be on the  $\text{KNO}_3$  saturation surface, that is, the solid phase would be potassium nitrate and the solution not saturated with sodium chloride.

A line drawn from  $N_1$  (representing mols of water to dissolve 1 mol  $\text{KNO}_3$ ) to the point  $b$  on the elevation is a path of crystallization on the  $\text{KNO}_3$  saturation surface. If a line is drawn from  $\text{NO}_3$  (representing  $\text{KNO}_3$ ) through a point vertically above  $a_1$  and produced, it will meet the line  $N_1b$  at a point representing the composition of the solution at  $25^{\circ}\text{C}$ . A slight excess of water therefore ensures the purity of the potassium nitrate.

If solution  $b$  instead of solution  $b_1$  were used to make the complex, the same point  $c$  would not be obtained, but if the correct proportion were used the difference would be very small. The line from  $O$  to  $b_1$  passes through  $c$  on the elevation, while a line from  $b$  to  $O$  passes very close to it. The proportions are, however, different. The proportions  $O, c$  of solution  $b_1$  and  $b_1, c$  of solid mixture  $O$  on the elevation are the same as those obtained from the line  $O, c, b$  on the plan. If solution  $b$  is used and no water removed then the proportions must be taken from the elevation,  $O, c$  of solution  $b$  and  $b, c$  of mixture  $O$ .

If solution  $b$  is used the volume of liquor will increase after each cycle of operations. On the other hand, some unavoidable evaporation will take place, some liquor will be lost and some removed from the process with the crystals.

A cycle of reactions has now been studied qualitatively for the conversion of sodium nitrate and potassium chloride into potassium nitrate and sodium chloride between two temperatures. Table 26 shows how the reactions may be followed quantitatively and an explanation of the method used is added. The compositions represented by the various points are as follows :

	KNO <sub>3</sub> .	NaCl.	NaNO <sub>3</sub>	Water.
<i>c</i> . . . . .	0.421	0.474	0.105	1.55 mols per mol of salts
<i>a</i> . . . . .	0.600	0.250	0.150	2.21 " " " " "
<i>a</i> <sub>1</sub> . . . . .	0.600	0.250	0.150	2.40 " " " " "
<i>b</i> . . . . .	0.304	0.435	0.261	4.20 " " " " "
<i>b</i> <sub>1</sub> . . . . .	0.304	0.435	0.261	3.84 " " " " "

TABLE 26

0.750 mol salts as complex *c* = 0.526 mol salts as solution *a* + 0.224 mol NaCl.

0.526 mol salts as solution *a* require 0.10 mol added water.

Mols per Mol of Salts.				
	KNO <sub>3</sub>	NaCl	NaNO <sub>3</sub>	Water.
0.750 mol salts as complex <i>c</i> . . . . .	0.316	0.355	0.079	1.16
0.224 mol NaCl removed . . . . .		0.224		
0.10 mol water added . . . . .				0.10
0.526 mol salts as solution <i>a</i> <sub>1</sub> . . . . .	0.316	0.131	0.079	1.26

0.526 mol salts as solution *a* = 0.302 mol salts as solution *b* + 0.224 mol KNO<sub>3</sub>.

0.302 mol salts as solution *b* require 0.10 mol water to be removed.

0.526 mol salts as solution <i>a</i> <sub>1</sub> . . . . .	0.316	0.131	0.079	1.26
0.224 mol KNO <sub>3</sub> removed . . . . .	0.224			
0.10 mol water removed . . . . .				0.10
0.302 mol salts as solution <i>b</i> <sub>1</sub> . . . . .	0.092	0.131	0.079	1.16

0.302 mol salts as solution *b*<sub>1</sub> + 0.448 mol mixture *O* = 0.750 mol salts as complex *c*.

0.302 mol salts as solution <i>b</i> <sub>1</sub> . . . . .	0.092	0.131	0.079	1.16
0.448 mol mixture <i>O</i> . . . . .	0.224	0.224		
0.750 mol salts as complex <i>c</i> . . . . .	0.316	0.355	0.079	1.16

EXPLANATION OF TABLE 26

The procedure might be as follows :—

The diagram is plotted on squared paper from the data given in Table 25. The point *a* is marked on the curve *EF* at 0.750 NO<sub>3</sub> and the plan is completed by drawing tie lines from NaCl to *a*, from KNO<sub>3</sub> through *a* to find *b* and from *b* to *O* to find *c*. On the elevation tie lines are drawn from Cl to *a*, from KNO<sub>3</sub> through *a* to find *b*<sub>1</sub>, from KNO<sub>3</sub> to *b* to find *a*<sub>1</sub> and from *O* to *b*<sub>1</sub> to find *c*.

The tie line, or path of crystallization, from NaCl to *a* passes through *c* and gives the proportion of solid NaCl and solution *a*. This line and its parts are conveniently measured along the base of the square and it will be found that NaCl to *a* measures 0.750 mol of salts as complex *c* and is divided into NaCl to *c* = 0.526 mol of salts as solution *a* and *a* to *c* = 0.224 mol of solid NaCl at 75° C. The

0.224 mol of NaCl is assumed to be removed leaving a solution containing 0.526 mol of salts as solution *a*.

The vertical distance *a* to *a*<sub>1</sub> is measured on the elevation to find the amount of water to be added to 1 mol of salts as solution *a* to move its composition into the KNO<sub>3</sub> field to a point which will allow it to remain in that field during the cooling to 25° C. The distance *a* to *a*<sub>1</sub> measures 0.19 mol water for 1 mol of salts as solution *a*, so 0.526 mol will require 0.10 mol water. The tie line from KNO<sub>3</sub> through *a* to *b* is conveniently measured along the NO<sub>3</sub> side of the square. The line measures 0.696 mol of salts as solution *a* and is made up of KNO<sub>3</sub> to *a* = 0.400 mol of salts as solution *b* and *b* to *a* = 0.296 mol KNO<sub>3</sub>. For 0.526 mol of salts as solution *a* (see above) there will be 0.302 mol of salts as solution *b* and 0.224 mol KNO<sub>3</sub>. The 0.224 mol of KNO<sub>3</sub> is assumed to be removed, leaving 0.302 mol of salts as solution *b* at 25° C.

The vertical distance from *b* to *b*<sub>1</sub> on the elevation is measured to find the amount of water to be removed. The distance measures 0.33 mol of water to be removed from 1 mol of salts as solution *b*. There is 0.302 mol of salts as solution *b*, so the amount of water to be removed is 0.1 mol which is the same as the amount added to solution *a*. The tie line from *b* to *O* on the plan measured vertically on the plan gives *O* to *c* = 0.079 mol of salts as solution *b* plus 0.117 mol of mixture *O*. (NaNO<sub>3</sub> + KCl) = 0.196 mol of salts in complex *c*. Therefore 0.302 mol of salts as solution *b* (see above) will need 0.448 mol of mixture *O* to be added to yield 0.750 mol of salts in complex *c*.

The cycle is now complete, it started with 0.750 mol complex *c* and it has finished with 0.750 mol of the same complex. 0.448 mol of mixture *O* (NaNO<sub>3</sub> + KCl) has been converted into 0.224 mol of KNO<sub>3</sub> and 0.224 mol of NaCl.

In Table 26 the quantities of salts and of water in mols is given in table form for one complete cycle.

The lengths of the paths of crystallization are best measured along one of the sides of the square. Thus the line NaCl through *c* to *a* may be measured along the edge of the square NaCl.NaNO<sub>3</sub> from NaCl. When the composition of *a* was read from the diagram the NaCl was read as 0.250 mol ; therefore the length of the line NaCl to *a* must be 0.750 mol. Thus the measurements of the lines are of the same degree of accuracy as the reading and plotting of the points, and one may be used to check the other. The point *c* was read as

TABLE 27

G.					Composition. %				
	KNO <sub>3</sub> .	NaCl.	NaNO <sub>3</sub> .	Water.	KNO <sub>3</sub> .	NaCl.	NaNO <sub>3</sub> .	Water.	
100.0 g. complex <i>c</i> =	39.7	25.9	8.3	26.1	39.7	25.9	8.3	26.1	
16.3 g. NaCl removed		16.3							
83.7 g. solution <i>a</i> =	39.7	9.6	8.3	26.1	47.5	11.4	9.9	31.2	
2.3 g. water added				2.3					
86.0 g. solution <i>a</i> <sub>1</sub> =	39.7	9.6	8.3	28.4	46.2	11.1	9.7	33.0	
28.1 g. KNO <sub>3</sub> removed	28.1								
57.9 g. solution <i>b</i> =	11.6	9.6	8.3	28.4	20.0	16.6	14.4	49.0	
2.3 g. water removed				2.3					
55.6 g. solution <i>b</i> <sub>1</sub> =	11.6	9.6	8.3	26.1	20.9	17.3	14.9	46.9	
44.4 g. mixture <i>O</i> added	28.1	16.3							
100.0 g. complex <i>c</i> =	39.7	25.9	8.3	26.1	39.7	25.9	8.3	26.1	



0.474 mol NaCl; therefore from NaCl to  $c$  must be 0.526 mol as solution  $a$ . The whole line reads:

0.750 mol as complex  $c = 0.526$  mol as solution  $a + 0.224$  mol of NaCl.

Table 27 has been calculated from the data in Table 26, and shows the same cycle of reactions but the quantities are in grammes and the compositions of the solutions in grammes per 100 g. of solution. This calculation is, of course, necessary before the findings of a phase

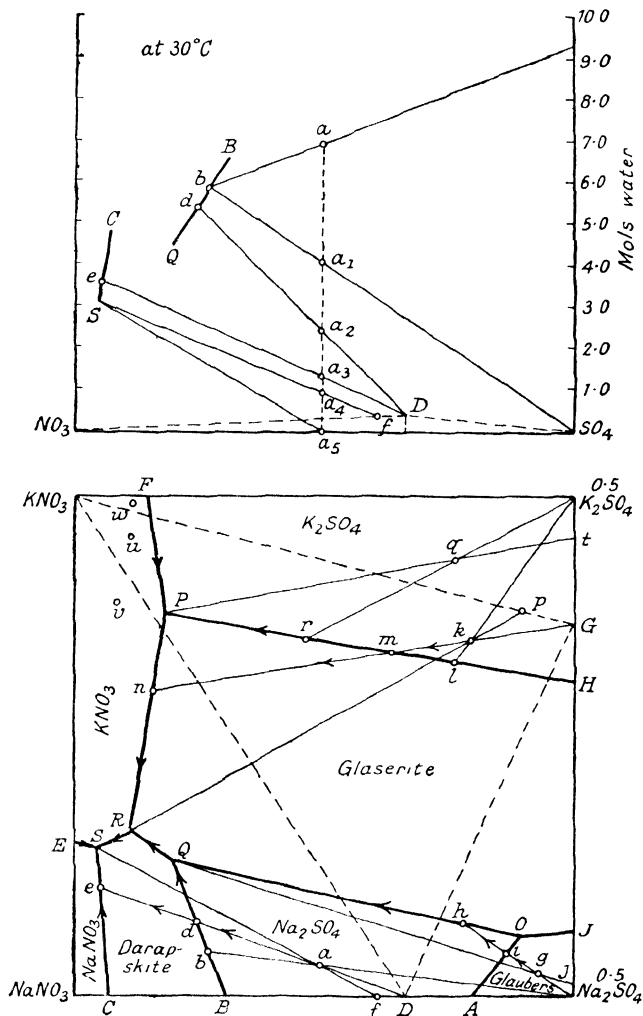


FIG. 37.

diagram study can be applied to practice. The data in terms of mols per mol of salts are converted first to grammes by multiplying each item by its molecular weight and then to per cent., by multiplying each item in grammes by 100 divided by the sum of all the items in grammes. One example should make this clear.

Complex *c* read from Fig. 36 has the following composition :

KNO <sub>3</sub> .	NaCl	NaNO <sub>3</sub>	Water
0.421	0.474	0.105	1.55 mols

This may be calculated to per cent. by weight as follows :

				g.			
KNO <sub>3</sub>	.	.	.	0.421 × 101	= 42.6	which, multiplied by	$\frac{100}{107.1} = 39.7\%$
NaCl	.	.	.	0.474 × 58.5	= 27.7	..	.. = 25.9%
NaNO <sub>3</sub>	.	.	.	0.105 × 85	= 8.9	..	.. = 8.3%
Water	.	.	.	1.55 × 18	= 27.9	..	.. = 26.1%
				107.1		100.0	

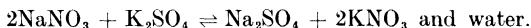
To find the weight of solid NaCl and of solution *b* in 100 g. of complex *c* :

From Table 26 : 0.224 mols of solid NaCl were removed from a quantity of complex *c* containing a total of 0.355 mols of NaCl. Therefore, 100 g. of complex *c* contain 25.9 g. of NaCl.

$$\frac{25.9 \times 0.224}{0.355} = 16.3 \text{ g. of NaCl removed.}$$

The weight of solution *b* is the difference, 100 — 16.3 = 83.7 g., as shown in Table 27. The weights of KNO<sub>3</sub> and of water may be found in the same way.

**Double Salts and Hydrates.** A reciprocal salt pair in its simpler form has been represented, and the reactions resulting from evaporation, dilution, heating and cooling have been studied on Jänecke's projection. It is now proposed to consider a more complicated case, and the system chosen is :

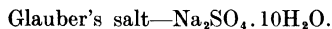


Figs. 37 and 38 show this system at 30° C. The two diagrams represent the same isotherm, but two figures have been prepared to avoid confusion of lines when tracing out a number of phase reactions. It should be observed that there are saturation surfaces representing two double salts, one anhydrous and one hydrated, and a hydrated simple salt in addition to the four salts given in the above equation.

The double salts are :

Glaserite—Na <sub>2</sub> SO <sub>4</sub> .3K <sub>2</sub> SO <sub>4</sub> or NaK <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> .	<i>G</i> on Figs. 37 and 38.
Darapskite—Na <sub>2</sub> SO <sub>4</sub> .NaNO <sub>3</sub> .H <sub>2</sub> O.	<i>D</i> on Figs. 37 and 38.

The hydrated simple salt is :



The diagram has been plotted from the data in Table 28. In calculating the data from grammes per 100 g. of solution to mols per mol of salts, the grammes of NaNO<sub>3</sub> and KNO<sub>3</sub> are divided by their respective molecular weights to obtain the number of mols. The grammes of Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> are divided by half their respective molecular weights

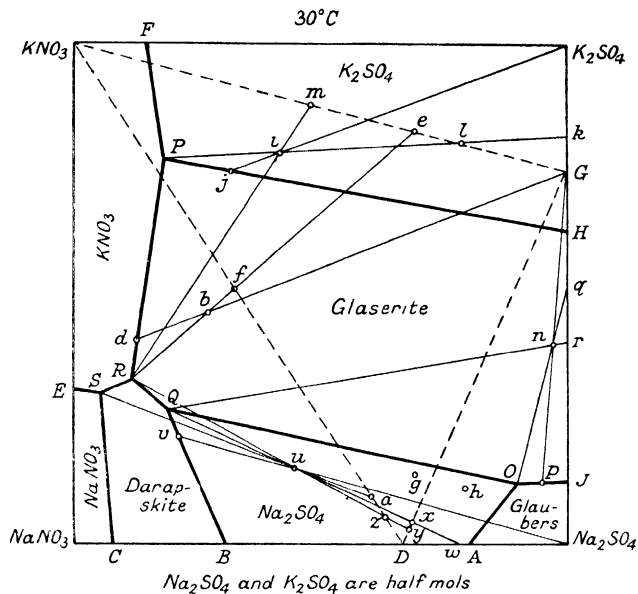


FIG. 38.

to obtain the number of half-mols. This is necessary because one equivalent of  $\text{Na}_2\text{SO}_4$  requires two equivalents of  $\text{KNO}_3$  to satisfy the equation. The table is therefore headed mols of  $\text{NaNO}_3$  and  $\text{KNO}_3$  but 0.5 mols of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ . The same object would have been achieved if the molecular weights of  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  had been used and twice the molecular weights of  $\text{NaNO}_3$  and  $\text{KNO}_3$ . In that case the mols of water would be doubled, and though that makes no difference to the phase diagram, it is necessary to be careful to use the same molecular weight for calculating the mols back to grammes as was used to calculate the grammes to mols. One example may be useful:

The point  $Q$  given as grammes per 100 g. solution has the following composition:

$\text{NaNO}_3$ %	$\text{Na}_2\text{SO}_4$ %	$\text{KNO}_3$ %	Water. %
28.0	8.04	16.1	47.9

The  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and water are divided by their molecular weights, and the  $\text{Na}_2\text{SO}_4$  is divided by half its molecular weight.

$\frac{28.0}{85} \text{ NaNO}_3$	$\frac{8.04}{71} \text{ Na}_2\text{SO}_4$	$\frac{16.1}{101} \text{ KNO}_3$	$\frac{47.9}{18} \text{ Water}$
= 0.330	= 0.113	= 0.159	= 2.66 mols.

The mols of salts, excluding the water, added together = 0.602; therefore the mols of salts and of water per mol of salts

= 0.330	0.113	0.159	2.66
= 0.602	0.602	0.602	0.602
= $\text{NaNO}_3$	0.5 $\text{Na}_2\text{SO}_4$	$\text{KNO}_3$	Water.
= 0.547	0.188	0.265	4.42

or

Na.	K.	0.5 $\text{SO}_4$ .	$\text{NO}_3$ .	Water.
0.735	0.265	0.188	0.812	4.42

TABLE 28

THE QUATERNARY SYSTEM,  $\text{NaNO}_3 \cdot \text{K}_2\text{SO}_4$ . WATER, FORMING THE  
 RECIPROCAL PAIR  $2\text{NaNO}_3 + \text{K}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + 2\text{KNO}_3$

Mols per Mol of Salts at 30° C.

Point.	$\text{KNO}_3$ .	0.5 $\text{K}_2\text{SO}_4$ .	$\text{NaNO}_3$ .	0.5 $\text{Na}_2\text{SO}_4$ .	Water.	Solid Phase.
<i>L</i>	1	—	—	—	12.50	$\text{KNO}_3$
<i>K</i>	—	—	1	—	4.92	$\text{NaNO}_3$
<i>M</i>	—	1	—	—	28.60	$\text{K}_2\text{SO}_4$
<i>N</i>	—	—	—	1	9.26	$\text{Na}_2\text{SO}_4$
<i>E</i>	0.303	—	0.697	—	3.17	$\text{KNO}_3 + \text{NaNO}_3$
<i>F</i>	0.860	0.140	—	—	11.37	$\text{KNO}_3 + \text{K}_2\text{SO}_4$
<i>H</i>	—	0.626	—	0.374	21.35	$\text{K}_2\text{SO}_4 + \text{Glaserite}$
<i>J</i>	—	0.136	—	0.864	7.75	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Glaserite}$
<i>A</i>	—	—	0.207	0.793	7.82	$\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
<i>B</i>	—	—	0.697	0.303	6.50	$\text{Na}_2\text{SO}_4 + \text{Darapskite}$
<i>C</i>	—	—	0.933	0.067	4.78	$\text{NaNO}_3 + \text{Darapskite}$
<i>S</i>	0.296	—	0.667	0.037	3.12	$\text{NaNO}_3 + \text{KNO}_3 + \text{Darapskite}$
<i>R</i>	0.323	—	0.573	0.104	3.75	$\text{KNO}_3 + \text{Darapskite} + \text{Glaserite}$
<i>Q</i>	0.265	—	0.547	0.188	4.42	$\text{Na}_2\text{SO}_4 + \text{Darapskite} + \text{Glaserite}$
<i>O</i>	—	0.117	0.095	0.788	7.33	$\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Glaserite}$
<i>P</i>	0.765	—	0.061	0.174	9.03	$\text{KNO}_3 + \text{K}_2\text{SO}_4 + \text{Glaserite}$
<i>G</i>	—	0.750	—	0.250	—	
<i>D</i>	—	—	0.333	0.667	0.333	

Data for the internal system are from E. Cornee, H. Krombach and A. Spack in *Caliche*, Aug. 1929.  
 The external systems are from various sources.

*G* gives composition of glaserite :  $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$ .

*D* „ „ „ darapskite :  $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

When plotting diagrams from data found in the literature, especially when the data are from more than one source, a good deal of calculation is often necessary. The data may be in grammes per 100 g. of solution, or per 100 g. of water, or these may be in mols per 1,000 mols of water or the mols may be mol ions. A good 10-inch slide rule is sufficiently accurate for all ordinary purposes, and with a little practice the re-calculation of the data can be carried out quite quickly. It may here be stated that the figures given throughout this book have generally been obtained by the use of the slide rule.

Inspection of the diagram, Fig. 37 or 38, shows that the system may be divided into four quaternary systems, one for each of the four drying-up points *P*, *Q*, *R* and *S*. These four systems are :

$\text{KNO}_3$ .Glaserite. $\text{K}_2\text{SO}_4$ .Water.	(Drying-up point <i>P</i> )
Darapskite.Glaserite. $\text{Na}_2\text{SO}_4$ .Water.	( „ „ „ „ <i>Q</i> )
$\text{KNO}_3$ .Darapskite.Glaserite.Water.	( „ „ „ „ <i>R</i> )
$\text{KNO}_3$ .Darapskite. $\text{NaNO}_3$ .Water.	( „ „ „ „ <i>S</i> )

The point *S* represents the only congruently saturated quaternary invariant solution at the temperature, so *S* is the final drying-up point of all quaternary solutions. *S* is the drying-up point of the system  $\text{KNO}_3$ .darapskite. $\text{NaNO}_3$ .water. It is the drying-up point

of the remaining systems only if the solid phase is removed, which in effect is moving the complex into the system named. The remaining invariant points  $P$ ,  $Q$  and  $R$  are incongruent drying-up points.  $P$  is the drying-up point of the system  $\text{KNO}_3$ .glaserite. $\text{K}_2\text{SO}_4$ .water, but it is situated outside the system although saturated with the three salt components of that system. In the same way  $Q$  is the incongruent drying-up point of the system

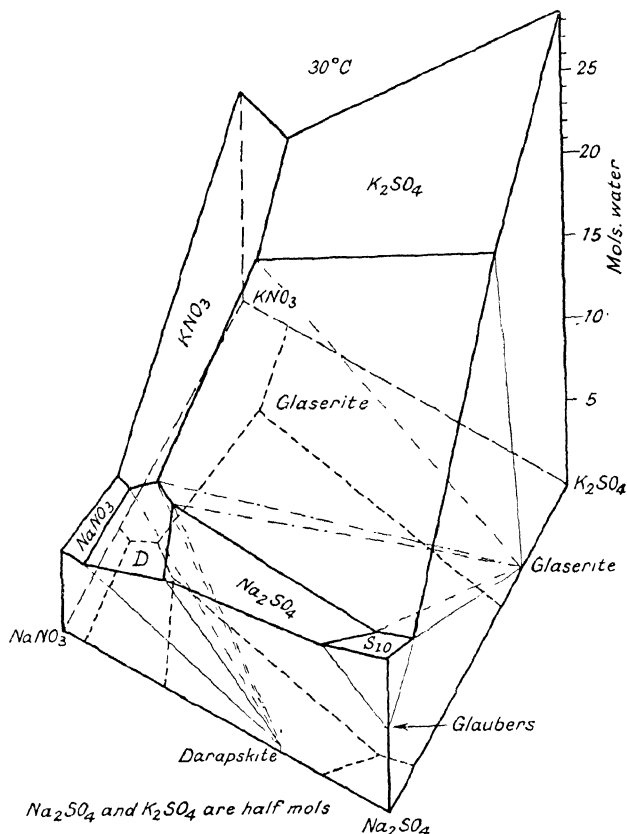


FIG. 39.

darapskite.glaserite. $\text{Na}_2\text{SO}_4$ .water, and  $R$  the incongruent drying-up point of the system  $\text{KNO}_3$ .darapskite.glaserite.water. The point  $O$  is not a drying-up point.

The isotherm has seven saturation surfaces, but it must be remembered that the *fields* are not surfaces but figures in space. Thus the saturation surface  $CSRQB$  represents darapskite, but the field of darapskite is a distorted and inverted pyramid with the surface  $CSRQB$  as its base and the point  $D$  as its apex (see Fig. 39), which is a perspective view including water. In the same way the surface  $BQOA$  is the saturation surface of  $\text{Na}_2\text{SO}_4$ .

which is the base of an inverted pyramid with the  $\text{Na}_2\text{SO}_4$  corner as the apex. On the plan projection, therefore, a point which appears to be on the  $\text{Na}_2\text{SO}_4$  saturation surface may be within the  $\text{Na}_2\text{SO}_4$  field or the darapskite field according to the amount of water present. This can be seen on the elevation of Fig. 37 where the point  $a$  lies on the  $\text{Na}_2\text{SO}_4$  saturation surface. On removing water to  $a_1$  the complex is within the  $\text{Na}_2\text{SO}_4$  field, but at  $a_2$  it has passed into the darapskite field.

There are four stable pairs of salts in the internal system:  $\text{KNO}_3$  and glaserite can exist together in equilibrium with solutions on the curve  $RP$ ;  $\text{KNO}_3$  and darapskite with solutions on the curve  $RS$ ; darapskite and glaserite with solutions on the curve  $RQ$  and glaserite and  $\text{Na}_2\text{SO}_4$  on the curve  $QO$ .

The paths of crystallization radiate from the four corners of the square and along the curves to the drying-up points, as was the case in the simple reciprocal salt pair diagrams. In the case of the double salts the paths radiate from the point representing the double salt and across its saturation surface. The arrows on the diagram make this clear.

The phase reactions involved when water is removed isothermally from the complex represented by the point  $a$  on Fig. 37 are as follows:  $a$  represents a solution just saturated with  $\text{Na}_2\text{SO}_4$ , and is therefore on the  $\text{Na}_2\text{SO}_4$  saturation surface. When water is removed the solution point moves away from  $\text{Na}_2\text{SO}_4$  and meets the curve  $BQ$  at  $b$ . The complex is now  $a_1$ , the solid phase is  $\text{Na}_2\text{SO}_4$  and the solution is  $b$  saturated with  $\text{Na}_2\text{SO}_4$  and darapskite.

Further removal of water from  $a_1$  to  $a_2$  on the elevation causes the solution point to move from  $b$  towards  $Q$ , and the solid phase to move from  $\text{Na}_2\text{SO}_4$  towards darapskite on the edge of the square. Actually  $\text{Na}_2\text{SO}_4$  goes into solution and darapskite is deposited, and when the solution point is at  $d$  the solid phase is all darapskite.

When more water is removed from  $a_2$  to  $a_3$  on the elevation, the solution point crosses the darapskite saturation surface because  $d$  lies on a path of crystallization from  $D$  through  $a$ , so that the solution point must leave the curve  $BQ$ . When the solution point reaches  $e$  the solution is saturated with darapskite and  $\text{NaNO}_3$ , but the solid phase is still all darapskite.

On the removal of water from  $a_3$  to  $a_4$  on the elevation, the solution point moves along the curve  $CS$  towards  $S$  and the solid phase moves from  $D$  towards  $\text{NaNO}_3$ . When the solution is represented by  $S$  the solid phase is a mixture of  $\text{NaNO}_3$  and darapskite represented by the point  $f$ . At composition  $S$  the solution dries up and the solid phase moves from  $f$  to  $a$  on the plan and from  $f$  to  $a_5$  on the elevation.

Having followed one series of reactions on both plan and elevation it is proposed to indicate other series in different parts of the isotherm but using the plan only.

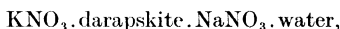
It might be repeated here that the reader should prepare larger diagrams on squared paper, using the data given in the tables. Squared paper ruled in inches and tenths is useful. Figs. 37 and 38 should be plotted on at least a 10-inch square and with an elevation of the curves required for the reaction being studied. Some of the examples should be worked out in full, first qualitatively and then quantitatively. Carrying out the various operations from the plotting of the diagram to the final calculations to grammes or pounds is the quickest way to become familiar with the use of phase diagrams.

The point  $u$  on Fig. 38 represents another complex on the  $\text{Na}_2\text{SO}_4$  saturation surface. On the removal of water the solution point moves away from  $\text{Na}_2\text{SO}_4$  and meets the curve  $BQ$  at  $v$ . On the further removal of water the solution point moves towards  $Q$  and the solid phase moves from  $\text{Na}_2\text{SO}_4$  towards darapskite and is at  $w$  when the solution point is at  $Q$ .

On continuing the evaporation of water the solution point remains at  $Q$ , a mixture of darapskite and glaserite is deposited while  $\text{Na}_2\text{SO}_4$  is dissolved. The solution point cannot leave  $Q$  until all the  $\text{Na}_2\text{SO}_4$  in the solid phase has passed into solution. During the evaporation of water from solution  $Q$  the composition of the solid phase moves from  $w$  to  $x$ , which represents a mixture of darapskite and glaserite ( $x$  being on the broken line joining  $D$  to  $G$ ).

As still more water is removed the solution point leaves  $Q$  and moves towards  $R$ , while the solid phase moves from  $x$  to  $y$  and is still a mixture of darapskite and glaserite;  $y$  is where the line  $Ru$  meets  $DG$ . On the further evaporation of water the solution point remains at  $R$ , darapskite and  $\text{KNO}_3$  are deposited and glaserite is dissolved until the composition of the solid phase moves from  $y$  to  $z$ , which is a mixture of  $\text{KNO}_3$  and darapskite. When all the glaserite has dissolved and the solid phase is at  $z$  the further removal of water causes the solution point to move from  $R$  to  $S$  and the point representing the solid phase moves from  $z$  to  $a$ . The removal of still more water causes solution  $S$  to dry up at composition  $S$ , while the solid phase moves from  $a$  to  $u$ .

Two cases have been considered when water was removed from a complex on the  $\text{Na}_2\text{SO}_4$  saturation surface. Both these cases were within the system



that is, the points  $a$  and  $u$  are both within the triangle representing that system.

The following is a summary of the phase reactions for the first case, complex  $a$ , Fig. 37.

Complex.	Solution.	Solid Phase (total).
$a$ to $a_1$	$a$ to $b$	$\text{Na}_2\text{SO}_4$
$a_1$ to $a_2$	$b$ to $d$	$\text{Na}_2\text{SO}_4$ to $D$
$a_2$ to $a_3$	$d$ to $e$	$D$
$a_3$ to $a_4$	$e$ to $S$	$D$ to $f$
$a_4$ to $a_5$	at $S$	$f$ to $a$

The path of crystallization crossed the darapskite surface and was  $a-b-d-e-S$ .

For the second case, complex  $u$ , Fig. 38, the phase reactions are summarized thus:

Complex	Solution	Solid Phase.
$u$ to $u_1$	$u$ to $v$	$\text{Na}_2\text{SO}_4$
$u_1$ to $u_2$	$v$ to $Q$	$\text{Na}_2\text{SO}_4$ to $w$
$u_2$ to $u_3$	at $Q$	$w$ to $x$
$u_3$ to $u_4$	$Q$ to $R$	$x$ to $y$
$u_4$ to $u_5$	at $R$	$y$ to $z$
$u_5$ to $u_6$	$R$ to $S$	$z$ to $a$
$u_6$ to $u_7$	at $S$	$a$ to $u$

The points  $u_1$  to  $u_7$  are on the elevation which is not given in Fig. 38. The path of crystallization followed the curves bounding the darapskite surface and was  $u-v-Q-R-S$ .

A straight line drawn from  $Q$  to  $D$  divides that part of the  $\text{Na}_2\text{SO}_4$  surface, within the system  $\text{KNO}_3, \text{darapskite}, \text{NaNO}_3, \text{water}$  into two parts. If the complex is on the sodium side of the line the path of crystallization will be similar to  $a-b-d-e-S$ , and if on the potassium side of the line the path will be similar to  $u-v-Q-R-S$ .

The remainder of the  $\text{Na}_2\text{SO}_4$  saturation surface falls partly within the system  $\text{KNO}_3$ .darapskite.glaserite.water and partly within the system

darapskite.glaserite. $\text{Na}_2\text{SO}_4$ .water.

If the point  $g$  is the complex, the path of crystallization will be similar to that when  $u$  was the complex, except that the solution will dry up at  $R$ . For the point  $h$  the path of crystallization will again be similar except that  $Q$  will be the drying-up point. In both cases if the solid phase is removed as formed the solution point will move to  $S$ .

The positions of  $u$ ,  $g$  and  $h$  might have been chosen so that the path of crystallization met the curve  $OQ$  instead of the curve  $BQ$ . In such cases the solution point would take a similar path except that it would move to  $Q$  along the curve  $OQ$  instead of the curve  $BQ$ , and the solid phase would move from  $\text{Na}_2\text{SO}_4$  towards glaserite instead of towards darapskite.

At the temperature of the isotherm there is a small field of Glauber's salt in the  $\text{Na}_2\text{SO}_4$  corner of the diagram. If in Fig. 37 the complex is represented by the point  $g$  on the Glauber's salt saturation surface, then the following is a summary of the phase reactions when water is removed.

Complex.	Solution.	Solid Phase.
$g$ to $g_1$	$g$ to $i$	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
$g_1$ to $g_2$	at $i$	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to $\text{Na}_2\text{SO}_4$
$g_2$ to $g_3$	$i$ to $h$	$\text{Na}_2\text{SO}_4$
$g_3$ to $g_4$	$h$ to $Q$	$\text{Na}_2\text{SO}_4$ to $j$
$g_4$ to $g_5$	at $Q$	$j$ to $g$

Here, again,  $g_1$  to  $g_5$  have not been marked on the elevation. The point  $g$  as solid phase represents a mixture of darapskite, glaserite and  $\text{Na}_2\text{SO}_4$ . The solution remains at  $i$  until all the Glauber's salt is converted to  $\text{Na}_2\text{SO}_4$ . The solution dries up at  $Q$  before all the  $\text{Na}_2\text{SO}_4$  can dissolve.

On the glaserite saturation surface the paths of crystallization radiate from  $G$  representing glaserite. In Fig. 38 the complex  $b$ , for example, may be on the saturation surface, that is, the solution is saturated with glaserite. On removing water the solution point will move in a direction away from  $G$  and meet the curve  $PR$  at  $d$ . The point  $d$  now represents the solution and  $G$  the solid phase. As more water is evaporated the composition of the solution moves from  $d$  to  $R$  and the composition of the solid phase moves from  $G$  to  $e$ . Solution  $d$  is saturated with glaserite and has become just saturated with  $\text{KNO}_3$ , glaserite alone being in the solid phase. As the solution point moves from  $d$  both glaserite and  $\text{KNO}_3$  are deposited, and when the solution point reaches  $R$  the solution which is saturated with glaserite and  $\text{KNO}_3$  is now also just saturated with darapskite. When still more water is removed the solution remains at  $R$ ,  $\text{KNO}_3$  and darapskite are deposited, but glaserite is dissolved so that the composition of the solid phase moves from  $e$  to  $f$ , being at  $f$  when all the glaserite has dissolved. On the further removal of water the solution point leaves  $R$  and moves towards  $S$ , while the composition of the solid phase moves from  $f$  towards  $D$  on the broken line  $\text{KNO}_3 \cdot D$  to a point near  $f$ . At composition  $S$  the solution dries up and the three salts  $\text{KNO}_3$ , darapskite and  $\text{NaNO}_3$  are deposited and the composition of the solid phase moves from near  $f$  to the complex point  $b$ .

The above description of the phase reactions when water is removed isothermally from the saturated solution represented by  $b$  has been given at some length as an example, but



it is proposed to deal with other complexes on the glaserite surface in summary form only. For example, the above case of the removal of water from complex *b*, Fig. 38, may be summarized as follows :

System  $\text{KNO}_3.D.\text{NaNO}_3.\text{water}$ . Glaserite saturation surface.

Path of crystallization from *G* through complex meets curve *PR*.

Solution.	Solid Phase.
Moves from complex to curve <i>PR</i> .	Glaserite.
Moves to <i>R</i> .	Glaserite + $\text{KNO}_3$ deposit. Point moves from <i>G</i> towards $\text{KNO}_3$ on line $\text{KNO}_3.G$ .
Remains at <i>R</i> .	$\text{KNO}_3$ + Darapskite deposit, Glaserite dissolves. Point moves to line $\text{KNO}_3.D$ .
Moves to <i>S</i> .	$\text{KNO}_3$ + Darapskite deposit. Point moves on line $\text{KNO}_3.D$ towards <i>D</i> .
Dries up at <i>S</i> .	$\text{KNO}_3$ + Darapskite + $\text{NaNO}_3$ deposit. Point moves to complex point.

The above summary covers all cases when the complex is on the glaserite surface and within the system  $\text{KNO}_3.D.\text{NaNO}_3.\text{water}$ , and in a position that a path of crystallization from *G* through the complex meets the curve *PR*.

The summaries given below indicate the phase reactions when the path of crystallization meets the curve *RQ* and *QO*.

System  $\text{KNO}_3.D.\text{NaNO}_3.\text{water}$ . Glaserite saturation surface.

Path of crystallization from *G* through complex meets curve *RQ*.

Solution.	Solid Phase.
Moves from complex to curve <i>RQ</i> .	Glaserite.
Moves to <i>R</i> .	Glaserite and Darapskite deposit. Point moves from <i>G</i> towards <i>D</i> on line <i>GD</i> .
Remains at <i>R</i> .	$\text{KNO}_3$ + Darapskite deposit, Glaserite dissolves. Point moves from line <i>GD</i> to line $\text{KNO}_3.D$ .
Moves to <i>S</i> .	$\text{KNO}_3$ + Darapskite deposit. Point moves on line $\text{KNO}_3.D$ towards $\text{KNO}_3$ .
Dries up at <i>S</i> .	$\text{KNO}_3$ + Darapskite + $\text{NaNO}_3$ deposit. Point moves to complex point.

Same system but path of crystallization from  $G$  meets curve  $QO$ .

Solution.	Solid Phase
Moves from complex to curve $QO$ .	Glaserite.
Moves to $Q$ .	Glaserite + $\text{Na}_2\text{SO}_4$ deposit. Point moves from $G$ towards $\text{Na}_2\text{SO}_4$
Remains at $Q$ .	Glaserite + Darapskite deposit, $\text{Na}_2\text{SO}_4$ dissolves. Point moves from side of square to line $GD$ .
Moves to $R$ .	Glaserite and Darapskite deposit. Point moves on line $GD$ towards $D$ .
Remains at $R$ .	$\text{KNO}_3$ + Darapskite deposit, Glaserite dissolves. Point moves from line $GD$ to line $\text{KNO}_3.D$ .
Moves to $S$ .	$\text{KNO}_3$ + Darapskite deposit. Point moves on line $\text{KNO}_3.D$ towards $\text{KNO}_3$ .
Dries up at $S$ .	$\text{KNO}_3$ + Darapskite + $\text{NaNO}_3$ deposit. Point moves to complex point.

The glaserite saturation surface extends over three systems: these are—

(1)  $\text{KNO}_3.D.\text{NaNO}_3$ .water, (2)  $\text{KNO}_3.G.D$ .water, and (3)  $D.G.\text{Na}_2\text{SO}_4$ .water.

Paths of crystallization drawn through complexes falling within the first of these three systems will meet one of the curves,  $PR$ ,  $RQ$  or  $QO$ . These three cases have already been described and summarized.

Paths of crystallization drawn through complexes falling within the second of the systems named will also meet one of the same three curves. The phase reactions start on the same lines as those described for the system  $\text{KNO}_3.D.\text{NaNO}_3$ .water, but the solution will dry up at  $R$  before all the glaserite has dissolved.

Within the third system, paths of crystallization from  $G$  will meet the curve  $QO$  or  $OJ$ , and in both cases the solution will dry up at  $Q$  before all the  $\text{Na}_2\text{SO}_4$  has dissolved. If the path of crystallization meets the curve  $QO$  the reactions are similar to those indicated in the third summary given above, except that the solution dries up at  $Q$  before all the  $\text{Na}_2\text{SO}_4$  has dissolved. The reactions involved if the path of crystallization meets the curve  $OJ$  are described below.

Let  $n$ , Fig. 38, be the complex on the glaserite saturation surface and within the system  $D.G.\text{Na}_2\text{SO}_4$ .water. When water is removed the solution point moves towards  $p$  and glaserite is deposited. From  $p$  the solution point moves towards  $O$ , glaserite and Glauber's salt being deposited and the composition of the solid phase moves from  $G$  towards  $q$  being at  $q$  when the solution is at  $O$ . As the removal of water continues the solution remains at  $O$ , glaserite and  $\text{Na}_2\text{SO}_4$  are deposited while Glauber's salt dissolves (or the Glauber's is converted into anhydrous sodium sulphate by the removal of water). The composition of the solid phase remains at  $q$  because the projection ignores water, but actually the point repre-

senting the solid phase moves vertically downwards in space until  $q$  represents a mixture of glaserite and  $\text{Na}_2\text{SO}_4$ . Then, when all the Glauber's salt has disappeared, the removal of more water causes the solution point to move from  $O$  to  $Q$ ; glaserite and  $\text{Na}_2\text{SO}_4$  are deposited, and the composition of the solid phase moves from  $q$  to  $r$  and as the solution dries up at  $Q$  the solid phase moves from  $r$  to  $n$ .

On the  $\text{K}_2\text{SO}_4$  saturation surface three examples,  $q$  and  $k$  of Fig. 37, and  $i$  of Fig. 38, are summarized below. In the first case the complex chosen, the point  $q$ , Fig. 37, is within the system  $\text{KNO}_3.G.\text{K}_2\text{SO}_4$ .water, so the drying-up point must be  $P$ . Thus to summarize :

Solution.	Solid Phase.
Moves from $q$ to $r$ .	$\text{K}_2\text{SO}_4$ .
Moves from $r$ to $P$ .	Glaserite deposits and $\text{K}_2\text{SO}_4$ dissolves. Point moves from $\text{K}_2\text{SO}_4$ to $t$ .
Dries up at $P$ .	$\text{KNO}_3$ and Glaserite are deposited, $\text{K}_2\text{SO}_4$ dissolves. Point moves from $t$ to $q$ .

The complex  $k$ , Fig. 37, is on the  $\text{K}_2\text{SO}_4$  saturation surface, but within the system  $\text{KNO}_3.G.D$ .water. The drying-up point must therefore be  $R$ , which is saturated with  $\text{KNO}_3$ , glaserite and darapskite. The phase reactions are summarized below :

Solution.	Solid Phase.
Moves from $k$ to $l$ .	$\text{K}_2\text{SO}_4$ .
Moves from $l$ to $m$ .	Glaserite deposits, $\text{K}_2\text{SO}_4$ dissolves. Point moves from $\text{K}_2\text{SO}_4$ to $G$ .
Moves from $m$ to $n$ across $G$ surface.	Glaserite deposits. Point remains at $G$ .
Moves from $n$ to $R$ .	$\text{KNO}_3$ and Glaserite deposit. Point moves from $G$ to $p$ on the line $\text{KNO}_3.G$ .
Dries up at $R$ .	$\text{KNO}_3$ and Darapskite deposit. Glaserite dissolves. Point moves from $p$ to $k$ .

The point  $k$  is on the sodium side of a line drawn from glaserite to  $P$ , the path of crystallization crossed the glaserite surface and was  $k m n R$ . Other complexes on the  $\text{K}_2\text{SO}_4$  surface and on the sodium side of the line named would follow a similar path.

The point  $i$ , Fig. 38, is on the  $\text{K}_2\text{SO}_4$  surface and within the system  $\text{KNO}_3.G.D$ .water, but it is on the potassium side of the line Glaserite- $P$ .

The following is a summary of the phase reactions :

Solution.	Solid Phase
Moves from <i>i</i> to <i>j</i> .	$K_2SO_4$ .
Moves from <i>j</i> to <i>P</i> .	Glaserite deposits, $K_2SO_4$ dissolves. Point moves from <i>k</i> to <i>l</i> .
Remains at <i>P</i> .	$KNO_3$ and Glaserite deposit, $K_2SO_4$ dissolves. Point moves from <i>k</i> to <i>l</i> .
Moves from <i>P</i> to <i>R</i> .	$KNO_3$ and Glaserite deposit. Point moves on line $KNO_3.G$ from <i>l</i> to <i>m</i> .
Dries up at <i>R</i> .	$KNO_3$ and Darapskite deposit, Glaserite dissolves. Point moves from <i>m</i> to <i>i</i> .

On the  $KNO_3$  surface, if the complex is in the system  $KNO_3.G.K_2SO_4$ .water, say at *v*, Fig. 37, the solution will dry up at *P*. If the complex is at *u*, Fig. 37, in the system  $KNO_3.D.G$ .water the solution will dry up at *R*, and if at *v*, Fig. 37, in the system  $KNO_3.D.NaNO_3$ .water the solution will dry up at *S*.

The  $NaNO_3$  and the darapskite surfaces are entirely within the system



and so all solutions will dry up at *S*.

A general rule has been illustrated above, namely, that when the path of crystallization is on the boundary of a field it can only enter that field when the solid phase is the phase of that field. For example, *d*, *m* and *i* of Fig. 37, where the solid phases are double salts (*D* or *G*) or a hydrate.

The phase reactions which take place when water is removed without change of temperature have now been studied in detail. The addition of water to the various solid mixtures results in the same reactions, but in the reverse order.

**Addition of a Salt.** The reactions resulting from the addition of solid salts to complexes, including solutions both saturated and unsaturated, should present no difficulties as long as the following principles are remembered.

The addition of the salt moves the point representing the complex in a straight line towards the point representing the added solid.

The addition or removal of water moves the point vertically, and the amount can be such that it moves into the required field representing a pure solid phase.

A line then drawn from the known solid phase through the complex gives the point representing the solution on the curve.

The solution point is not on the curve except with the correct amount of water, therefore the solution point must be considered on the elevation as well as on the plan.

Take any point within the square diagram to represent a solution or mixture. By adding one or more of the four salts the complex may be moved into any of the fields as represented on the square. By adding or removing water the point may be moved vertically into, or to the boundary of, the three-dimensional field representing the pure salt required.

The addition of a salt or of a solution of a salt or salts, providing the salt or salts are represented in the system, may be considered as doing no more than moving the complex (i.e. the particular system being studied). When the complex has been moved to its new position the problem then resolves itself into no more than the adjustment of the water, and it is for this reason that the examples of removal of water have been considered in such detail.

**Changing the Temperature.** The changing of temperature, the removal and addition of water and of salt were considered at some length when a complete cycle of operations was studied earlier in this chapter. It is not, therefore, proposed to consider isotherms for other temperatures for the system  $\text{NaNO}_3 + \text{K}_2\text{SO}_4$  and water. On the other hand, there are some interesting phase reactions which take place with change of temperature, and these might be considered briefly.

The curve  $AO$  on Fig. 38 (at  $30^\circ\text{C}$ .) separates the  $\text{Na}_2\text{SO}_4$  and Glauber's salt saturation surfaces. At a lower temperature, say  $20^\circ\text{C}$ ., the  $\text{Na}_2\text{SO}_4$  surface will have disappeared and sodium sulphate will be represented only as Glauber's salt. The reactions which take place as the temperature is lowered will now be described.

It is possible, by applying the principle of Le Chatelier, to predict the direction the phase reaction will take when temperature is altered. (See page 54.) By this principle, if heat is removed from the system, the phase reactions will be such that heat will be given out. That is, sodium sulphate will dissolve and Glauber's salt will be deposited; or, in other words, sodium sulphate will combine with water to form Glauber's salt; both these reactions are exothermic.

The removal of heat causes the temperature to fall and the curve  $AO$  moves towards the curve  $BQ$ , and the points  $A$  and  $B$  unite near  $B$  at  $24.3^\circ\text{C}$ . Below this temperature the curve  $AO$ , now  $BO$ , continues to move in the same general direction and below  $24.3^\circ\text{C}$ ., but above  $21.8^\circ\text{C}$ . forms a small triangle in the corner of the  $\text{Na}_2\text{SO}_4$  surface near  $Q$ . As the temperature falls still further this triangle gets smaller and smaller until at  $21.8^\circ\text{C}$ . it vanishes to a point. This new point near  $Q$  represents a solution saturated as to four solid phases, Glauber's salt, darapskite, glaserite and  $\text{Na}_2\text{SO}_4$ . These four solid phases can exist in equilibrium with a solution only at this temperature,  $21.8^\circ\text{C}$ .

The point near  $Q$  is a system invariant point and has no degree of freedom in the condensed system.

If the system is maintained at equilibrium the temperature will remain at  $21.8^\circ\text{C}$ . and the composition of the solution will remain unchanged until all the  $\text{Na}_2\text{SO}_4$  has disappeared, even if more heat is removed. When the  $\text{Na}_2\text{SO}_4$  has disappeared a degree of freedom is gained, the temperature will fall and the new solution, represented by a point near  $Q$ , will be saturated as to Glauber's salt, darapskite and glaserite.

If more heat is now removed from the system the temperature will fall and the composition of the solution will depend on the temperature. As the temperature falls the two points  $Q$  and  $R$  will move closer together until at  $17.6^\circ\text{C}$ . they will unite at a point representing a solution saturated as to Glauber's salt, darapskite, glaserite and  $\text{KNO}_3$ . This is a new system invariant point.

Above  $17.6^\circ\text{C}$ . there was a curve  $QR$  dividing the glaserite and the darapskite saturation surfaces. That is, glaserite and darapskite formed a stable pair, and Glauber's salt and  $\text{KNO}_3$  formed an unstable pair.

Below  $17.6^\circ\text{C}$ . the point formed by the union of  $Q$  and  $R$  again divides, and two new points appear, one on either side of the position occupied by the curve  $QR$  just before it

disappeared. This means that below  $17.6^{\circ}\text{C}$ . Glauber's salt and  $\text{KNO}_3$  become the stable pair, and glaserite and darapskite become the unstable pair.

To make this quite clear, at  $17.6^{\circ}\text{C}$ . four curves meet at a point which is in contact with four saturation surfaces. Both above and below  $17.6^{\circ}\text{C}$ . the point divides so that each new point is the junction of three curves. This example should be compared with the example given above when a system invariant point was formed near  $Q$  by the disappearance of the triangular field of  $\text{Na}_2\text{SO}_4$ . It will then be seen that there are two types of system invariant points in this condensed quaternary system. In all there are five such points between the temperatures of  $10^{\circ}\text{C}$ . and  $60^{\circ}\text{C}$ .

These are :

At  $10^{\circ}\text{C}$ ., when darapskite disappears and at  $21.8^{\circ}\text{C}$ . when  $\text{Na}_2\text{SO}_4$  disappears.

At  $60^{\circ}\text{C}$ . when darapskite +  $\text{KNO}_3$  form the stable pair below  $60^{\circ}\text{C}$ ., and  $\text{NaNO}_3$  +  $\text{Na}_2\text{SO}_4$  form the stable pair above  $60^{\circ}\text{C}$ . At  $44^{\circ}\text{C}$ . when darapskite + glaserite form the stable pair below  $44^{\circ}\text{C}$ ., and  $\text{Na}_2\text{SO}_4$  +  $\text{KNO}_3$  form the stable pair above  $44^{\circ}\text{C}$ . At  $17.6^{\circ}\text{C}$ . when Glauber's salt +  $\text{KNO}_3$  form the stable pair below  $17.6^{\circ}\text{C}$ ., and darapskite + glaserite form the stable pair above  $17.6^{\circ}\text{C}$ .

The data for plotting the isotherms necessary for the study of this system over the range of temperatures given above may be found in *Caliche*, July 1928 and August 1929. (Cornec, Krombach and Spack, Strasbourg University.)

## CHAPTER XII

### THE FIVE-COMPONENT SYSTEM : FOUR SALTS AND WATER

The representation of phase equilibrium data on a diagram becomes more complicated as more components are introduced. Thus, for the binary system it was possible to include temperature on a plane diagram. For the ternary system temperature had to be eliminated as a variable and isotherms were used ; the three components were represented in two dimensions by the artifice of triple co-ordinates. Temperature was of course included by superimposing a number of isotherms on the same diagram.

For the quaternary system three dimensions were necessary to represent all four components on isotherms. Thus, where the three salts had a common ion the system was represented within a tetrahedron, which was only briefly described at the end of Chapter VII ; where the salts had no common ion and thus formed a reciprocal salt pair, the system was represented within a square-based pyramid, such as Fig. 24. This was converted to a plane diagram, not by fixing the water composition as in the case of temperature for the ternary isotherm, but by ignoring water or leaving it off the diagram by projecting from the water point as in Jänecke's projection, e.g. Fig. 30.

The quinary system of four salts and water would similarly require four dimensions to represent the five components, that is, providing the triple co-ordinate device is still used. Thus one component has to be eliminated to enable the system to be represented even within a three-dimensional figure. Water is the component usually eliminated as was done for the quaternary. Here, again, the four salts may have a common ion, in which case the figure becomes a tetrahedron with one salt at each corner, or the four salts may not have a common ion throughout, in which case the figure has to include some square faces to represent reciprocal salt pairs. The salts in the latter case are also represented at the corners of the solid figure but, although there are only four components (apart from water), there are more than four salts. This was explained in the introduction to the reciprocal salt pair.

**Four Salts with a Common Ion.** The isotherm with water eliminated for the system of four salts with a common ion may, as already stated, be represented within a tetrahedron. This space model is built up from four quaternary systems which form the external faces of the space diagram. Each quaternary system is in a triangle (i.e. in two dimensions) obtained by making a Jänecke's projection on the base of the original quaternary tetrahedron with water at the apex or point of projection. Four salts and water can be arranged to make four quaternary systems, each of three salts and water : thus *A, B, C* and *D* can be taken as *ABC, BCD, CDA* and *DAB*. It is therefore clear that the four quaternary systems represented on triple co-ordinates can be combined to form the four-sided figure, the tetrahedron to represent the quinary system of four salts and water.

Each quaternary system will have a quaternary invariant point (i.e. when the systems are of the simplest type without hydrates or double salts). This is where the three equilibrium curves from the edges meet in the middle of the triangle. Two solid phases are in equilibrium along the curves, but three<sup>1</sup> are in equilibrium at the quaternary<sup>1</sup> invariant point, which is on the face of each side of the tetrahedron.

<sup>1</sup> Quaternary invariant point because there are four components altogether, three salts and water.

Within the tetrahedron there will be a quinary invariant point representing a solution saturated with respect to all four salts, and from this point four curves will radiate to meet the four quaternary invariant points of the four external systems.

This simple type of quinary system is unusual and is rarely likely to be encountered for practical investigations. It is not, therefore, proposed to consider it in any further detail.

**Quinary Systems with Reciprocal Salt Pairs.** Just as the reciprocal salt pairs are the important quaternary systems, so the more important and useful type of quinary system is one made up of three reciprocal salt pairs and two quaternary systems with

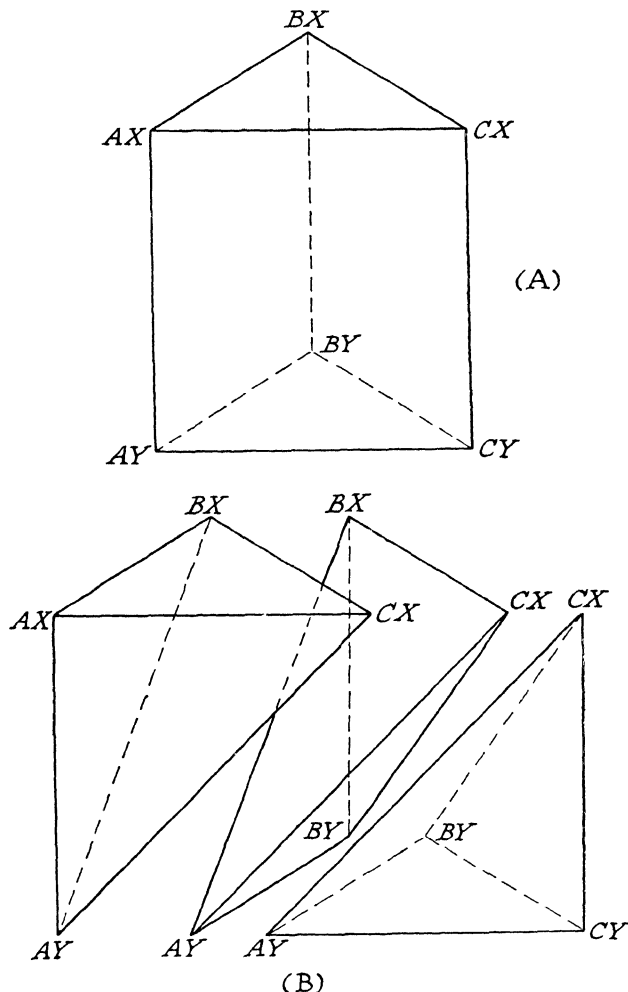


FIG. 40.



a common ion. The three squares and the two equilateral triangles used to represent the five "external" systems thus form the five surfaces of a regular triangular prism, the six corners representing six salts, although the system only comprises five components including water. This means that, although six salts are named and exist, any composition could be expressed in terms of four salts only.

Fig. 40A shows such a figure, and it will be noticed that each salt is linked to three other salts by the edges of the solid figure and that one of the three has a common anion while the other two have a common cation, or *vice versa*.

A further indication of why the system is quinary may now be given. The reciprocal salt pair had four salts and water and yet was quaternary because it could be divided by the diagonal into two systems each of three salts and water. Similarly, Fig. 40A can be divided, not into two triangles by one line but into three tetrahedra by two planes, see Fig. 40B. Any quinary point, that is inside the three-dimensional figure, can be represented in terms of the four salts at the four corners of one or other of the three tetrahedra.

The system in its simpler form would have three quinary invariant points, and in its simplest form the invariant points would be one in each of the three tetrahedra shown in Fig. 40B. From these points, representing solutions saturated as to four salts, four quinary curves would radiate to quaternary invariant points on the four faces of each tetrahedron. The two curves which join the three quinary invariant points are made up of the four curves which radiate from these invariant points to the inner faces of the tetrahedra, formed by the two cutting planes; the four short curves form two continuous curves joining the three points. That is, there are ten curves within the figure and these curves, together with the quaternary curves of the external systems, form the edges of surfaces which divide the whole figure into six fields, one for each of the six salts at the six corners of the prism.

On Fig. 40B, the internal plane surfaces already mentioned above are:  $BX.CX.AY$  forming one surface of the left-hand tetrahedron and one surface of the central tetrahedron;  $CX.BY.AY$  forming one surface of the right-hand and one of the central tetrahedron. These surfaces can be quaternary systems within the quinary system, just as in the quaternary system, see Fig. 33, the diagonal of the square formed a true ternary system.

In the simple quinary system now being considered, the surfaces  $BX.CX.AY$  and  $CX.BY.AY$  are true quaternary systems, three salts and water, and each tetrahedron is a quinary system, four salts and water, bounded by four quaternary systems, three salts and water. In practice such a simple quinary system is not likely to be found, as it involves the assumption of no double salts and that the three invariant points are all congruently saturated.

Only a few systems of four salts and water have been investigated to any degree of completeness. The classic example is the work of van't Hoff and his collaborators on the evaporation of sea water and on the salts of dried-up seas. Some of this work was on the system containing Na, K, Mg, Cl,  $SO_4$ , water, and many double salts were encountered. More recently the system Na, K,  $SO_4$ ,  $NO_3$ , Cl, water has been investigated very fully and at temperatures from 0°C. to 90°C. by E. Cornec, H. Krombach and A. Spack at the University of Strasbourg. This system makes a good example for a first study because it is fairly simple at the higher temperatures when only one double salt, glaserite, is found. The data are given in Table 29.

TABLE 29

THE QUINARY SYSTEM : SODIUM, POTASSIUM, SULPHATE, NITRATE, CHLORIDE, WATER at 75° C.  
Mols per Mol of Salts.

(Adapted from E. Cornec and H. Krombach, *Caliche*, Sept. 1928)

Ref.	Na.	K.	0.5SO <sub>4</sub> .	NO <sub>3</sub> .	Cl.	Water.	Solid Phase.
A <sub>1</sub>	1	—	—	1	—	3.33	NaNO <sub>3</sub>
B <sub>1</sub>	1	—	—	—	1	8.53	NaCl
C <sub>1</sub>	1	—	1	—	—	9.07	Na <sub>2</sub> SO <sub>4</sub>
D <sub>1</sub>	—	1	1	—	—	23.47	K <sub>2</sub> SO <sub>4</sub>
E <sub>1</sub>	—	1	—	—	1	8.33	KCl
F <sub>1</sub>	—	1	—	1	—	3.67	KNO <sub>3</sub>
A <sub>2</sub>	1	—	—	0.821	0.179	3.31	NaNO <sub>3</sub> + NaCl
B <sub>2</sub>	1	—	0.129	—	0.871	7.98	Na <sub>2</sub> SO <sub>4</sub> + NaCl
C <sub>2</sub>	0.820	0.180	1	—	—	7.55	Na <sub>2</sub> SO <sub>4</sub> + G
D <sub>2</sub>	0.300	0.700	1	—	—	16.15	K <sub>2</sub> SO <sub>4</sub> + G
E <sub>2</sub>	—	1	0.036	—	0.964	8.44	K <sub>2</sub> SO <sub>4</sub> + KCl
F <sub>2</sub>	—	1	—	0.675	0.325	3.41	KNO <sub>3</sub> + KCl
H <sub>2</sub>	—	1	0.025	0.975	—	3.63	KNO <sub>3</sub> + K <sub>2</sub> SO <sub>4</sub>
I <sub>2</sub>	1	—	0.037	0.963	—	3.25	NaNO <sub>3</sub> + Na <sub>2</sub> SO <sub>4</sub>
J <sub>2</sub>	0.550	0.450	—	—	1	6.91	NaCl + KCl
K <sub>2</sub>	0.538	0.462	—	1	—	1.50	NaNO <sub>3</sub> + KNO <sub>3</sub>
A <sub>3</sub>	1	—	0.030	0.800	0.170	3.25	NaNO <sub>3</sub> + Na <sub>2</sub> SO <sub>4</sub> + NaCl
B <sub>3</sub>	—	1	0.013	0.666	0.321	3.39	KNO <sub>3</sub> + K <sub>2</sub> SO <sub>4</sub> + KCl
C <sub>3</sub>	0.535	0.465	—	0.920	0.080	1.49	NaNO <sub>3</sub> + KNO <sub>3</sub> + NaCl
D <sub>3</sub>	0.378	0.622	—	0.727	0.273	2.34	KNO <sub>3</sub> + NaCl + KCl
E <sub>3</sub>	0.740	0.260	0.150	—	0.850	6.78	Na <sub>2</sub> SO <sub>4</sub> + NaCl + G
F <sub>3</sub>	0.550	0.450	0.050	—	0.950	6.34	NaCl + KCl + G
H <sub>3</sub>	0.140	0.860	0.050	—	0.950	7.92	KCl + K <sub>2</sub> SO <sub>4</sub> + G
I <sub>3</sub>	0.528	0.472	0.020	0.980	—	1.49	NaNO <sub>3</sub> + KNO <sub>3</sub> + Na <sub>2</sub> SO <sub>4</sub>
J <sub>3</sub>	0.492	0.508	0.028	0.972	—	1.74	Na <sub>2</sub> SO <sub>4</sub> + KNO <sub>3</sub> + G
K <sub>3</sub>	0.103	0.897	0.033	0.967	—	3.30	KNO <sub>3</sub> + K <sub>2</sub> SO <sub>4</sub> + G
A <sub>4</sub>	0.537	0.463	0.018	0.904	0.078	1.47	NaNO <sub>3</sub> + KNO <sub>3</sub> + NaCl + Na <sub>2</sub> SO <sub>4</sub>
B <sub>4</sub>	0.504	0.496	0.024	0.863	0.113	1.70	KNO <sub>3</sub> + NaCl + Na <sub>2</sub> SO <sub>4</sub> + G
C <sub>4</sub>	0.370	0.630	0.017	0.714	0.269	2.31	KNO <sub>3</sub> + NaCl + KCl + G
D <sub>4</sub>	0.133	0.867	0.017	0.673	0.310	3.10	KNO <sub>3</sub> + KCl + K <sub>2</sub> SO <sub>4</sub> + G

G = Glaserite : 3K<sub>2</sub>SO<sub>4</sub>.Na<sub>2</sub>SO<sub>4</sub>.

The Quinary System, Na.K.SO<sub>4</sub>.NO<sub>3</sub>.Cl. Water at 75° C.<sup>1</sup> The projection of the prism, Fig. 41, is a pictorial representation, and the internal system is only approximate to the data given in Table 29. The alterations were made for clarity. The figure is assumed to be made of wire and has one of the squares as base for convenience of viewpoint. The suffixes to the letters indicate the number of solid phases in equilibrium with the solution. There are four quinary invariant points (isothermal condensed) in the internal system, A<sub>4</sub>, B<sub>4</sub>, C<sub>4</sub> and D<sub>4</sub>. The curves radiating from these points to the external system link up with the curves of the external systems and form the boundaries of surfaces which divide the figure into seven three-dimensional fields, one for each possible solid phase, KNO<sub>3</sub>, NaNO<sub>3</sub>, KCl, NaCl, K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and glaserite.

The diagram, Fig. 42, is the same as Fig. 41, except that it is drawn to a smaller scale and the seven fields have been separated for greater clarity. Each field can now be studied separately and one or two examples should suffice.

SO<sub>4</sub> is of course 0.5 mol if the others are 1 mol.

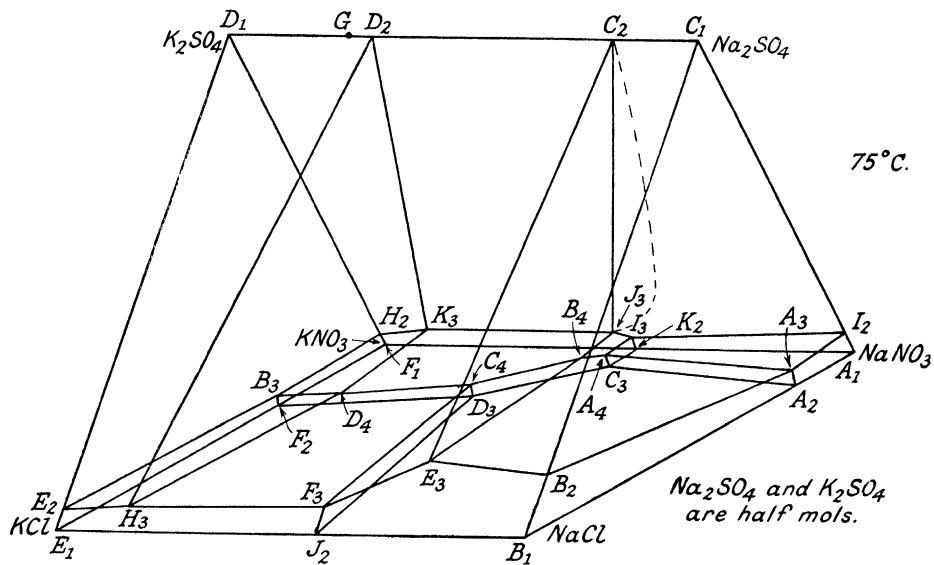


FIG. 41.

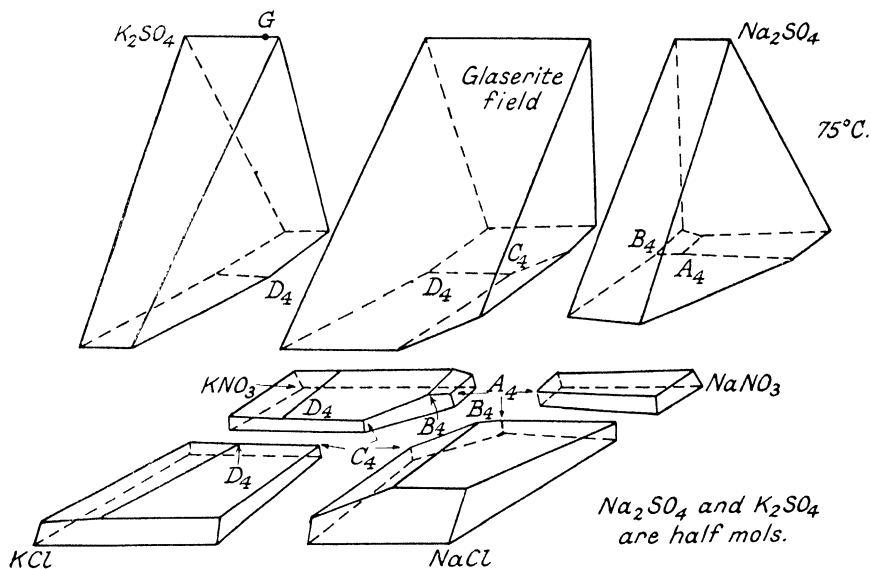


FIG. 42.

The small wedge-shaped field at the  $\text{NaNO}_3$  corner is the sodium nitrate field. This field has three internal faces, one which joins the sodium chloride field, the face at the narrow end which joins the potassium nitrate field, and the top face which joins the sodium sulphate field. Points on these three faces represent solutions saturated as to  $\text{NaNO}_3$  plus  $\text{NaCl}$ ,  $\text{NaNO}_3$  plus  $\text{KNO}_3$  and  $\text{NaNO}_3$  plus  $\text{Na}_2\text{SO}_4$ , respectively. *Internal surfaces, junction of two fields, represent solutions saturated as to two salts.* The remaining three faces are planes and belong to the external systems and points on these faces or inside the three-dimensional field represent solutions saturated with sodium nitrate.

The three internal edges, i.e. the curves radiating from the point  $A_4$ , are each curves of three salts, the longest curve, from  $A_4$  to the right represents solutions saturated as to  $\text{NaNO}_3$  plus  $\text{Na}_2\text{SO}_4$  plus  $\text{NaCl}$ , the shorter curve, from  $A_4$  represents solutions saturated as to  $\text{NaNO}_3$  plus  $\text{Na}_2\text{SO}_4$  plus  $\text{KNO}_3$  and the shortest curve, from  $A_4$  to the base of the figure, represents solutions saturated as to  $\text{NaNO}_3$  plus  $\text{NaCl}$  plus  $\text{KNO}_3$ . *Internal curves, junctions of three fields, represent solutions saturated as to three salts.*

The point  $A_4$  is at the junction of four fields and represents an invariant (isothermal condensed) quinary solution saturated as to  $\text{NaNO}_3$  plus  $\text{NaCl}$  plus  $\text{Na}_2\text{SO}_4$  plus  $\text{KNO}_3$ . As will be seen later the point  $A_4$  is congruently saturated and the  $\text{NaNO}_3$  field represents the simplest possible field in a quinary system. The potassium nitrate field at the left-hand top corner of the base in Fig. 41 is less simple and has three top faces, because, in addition to the  $\text{K}_2\text{SO}_4$  surface on the left, it has a glaserite surface and also the  $\text{Na}_2\text{SO}_4$  field overlaps the  $\text{KNO}_3$  field at the narrow end on the right forming a small  $\text{Na}_2\text{SO}_4$  surface.

The internal surfaces of the  $\text{KNO}_3$  field represent solutions saturated as to two salts as follows :—

Top surface on the left . . . .	$\text{KNO}_3 + \text{K}_2\text{SO}_4$
Top surface central position . . . .	$\text{KNO}_3 + \text{Glaserite}$
Top surface on the right . . . .	$\text{KNO}_3 + \text{Na}_2\text{SO}_4$
Surface joining $\text{KCl}$ field . . . .	$\text{KNO}_3 + \text{KCl}$
Surface joining $\text{NaCl}$ field . . . .	$\text{KNO}_3 + \text{NaCl}$
Surface joining $\text{NaNO}_3$ field . . . .	$\text{KNO}_3 + \text{NaNO}_3$

The internal curves of the  $\text{KNO}_3$  field represent solutions saturated as to three salts as follows :

The three curves radiating from the point  $A_4$  have already been mentioned for the  $\text{NaNO}_3$  field.

The curve from $A_4$ to $B_4$ . . . .	$\text{KNO}_3 + \text{NaCl} + \text{Na}_2\text{SO}_4$
The curve from $B_4$ to back of figure . . . .	$\text{KNO}_3 + \text{Na}_2\text{SO}_4 + \text{Glaserite}$
The curve from $B_4$ to $C_4$ . . . .	$\text{KNO}_3 + \text{NaCl} + \text{Glaserite}$
The curve from $C_4$ to $D_4$ . . . .	$\text{KNO}_3 + \text{KCl} + \text{Glaserite}$
The curve from $D_4$ to left of figure . . . .	$\text{KNO}_3 + \text{KCl} + \text{K}_2\text{SO}_4$

The points  $B_4$ ,  $C_4$  and  $D_4$  represent solutions saturated as to four salts as follows :

The point $B_4$ . . . .	$\text{KNO}_3 + \text{NaCl} + \text{Na}_2\text{SO}_4 + \text{Glaserite}$
The point $C_4$ . . . .	$\text{KNO}_3 + \text{NaCl} + \text{KCl} + \text{Glaserite}$
The point $D_4$ . . . .	$\text{KNO}_3 + \text{KCl} + \text{K}_2\text{SO}_4 + \text{Glaserite}$

Having followed the meaning of surfaces, curves and points on two of the fields the remaining five fields should present no difficulties.

Fig. 43 is the same view of the prism as was given in Fig. 41, but the prism has been divided into four tetrahedra by means of three planes. This figure should be compared with Fig. 40 A and B when the prism was divided into three tetrahedra. The reason for four tetrahedra in Fig. 43 is that another salt, glaserite, is present and glaserite is now one

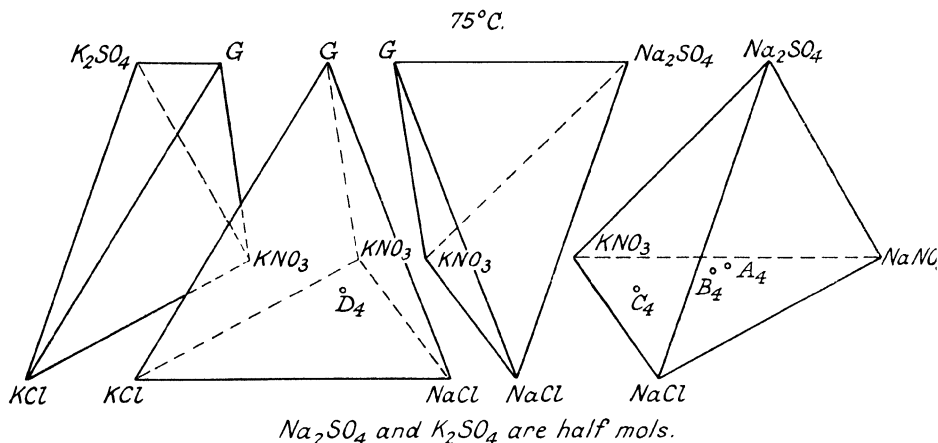


FIG. 43.

of the possible components. The system is still one of five components, four salts and water and the seven salts  $KNO_3$ ,  $NaNO_3$ ,  $KCl$ ,  $NaCl$ ,  $K_2SO_4$ ,  $Na_2SO_4$  and glaserite may be represented by equations in terms of the four salts at the four corners of any one of the tetrahedra, negative terms and zero terms being allowed.

The four quinary invariant points have been marked within the tetrahedra on Fig. 43; compare this with Fig. 41, for which purpose the same letters have been used. The positions of these four points will now be considered. The point  $A_4$  is within the tetrahedron which represents the system  $NaNO_3 \cdot NaCl \cdot Na_2SO_4 \cdot KNO_3$  and water, and the point  $A_4$  is also saturated with the four salts just named. That is, the solution can exist in equilibrium with solid  $NaNO_3$ ,  $NaCl$ ,  $Na_2SO_4$  and  $KNO_3$ , and it can be represented in positive terms of those four salts. The solution represented by point  $A_4$  is, therefore, congruently saturated and is the drying-up point of the system within which it is situated. As will be seen later, it is also the final drying-up point of the whole system represented within the prism.

The points  $B_4$  and  $C_4$  are also within the tetrahedron representing the system  $NaNO_3 \cdot NaCl \cdot Na_2SO_4 \cdot KNO_3$  and water. The point  $B_4$  is saturated as to  $KNO_3$  plus  $NaCl$  plus  $Na_2SO_4$  plus glaserite, and cannot be represented in positive terms of the components of the system. It represents a solution incongruently saturated. In a similar way, the point  $C_4$  is incongruently saturated.

The point  $D_4$  represents a solution saturated as to  $KNO_3$ ,  $KCl$ ,  $K_2SO_4$  and glaserite, but is within the system with  $KNO_3 \cdot NaCl \cdot KCl \cdot glaserite$  as components. Solution  $D_4$  is, therefore, incongruently saturated.

The points  $A_4$ ,  $B_4$ ,  $C_4$  and  $D_4$  are all drying-up points. If water is removed isothermally



be deposited and glaserite will dissolve. If the solid phases are removed or all the glaserite is dissolved the composition of the solution will change and will move from  $B_4$  to  $A_4$ .

At  $A_4$  the composition of the solution remains unchanged during isothermal evaporation right down to dryness, and the composition of solution and of the solid phase is the same.  $A_4$  is the final drying-up point of the whole system.

**Plotting the Diagram within the Prism.** A convenient projection of the prism to use when plotting the diagram is shown in Fig. 44. Five of the edges of the prism are each the length of a side of the square and four of them are the length of half a diagonal. Each edge is considered to be divided into 100 parts, but it is more convenient to draw the projection of the prism in, say, inches, and then to use a scale in inches and tenths to mark off the points. When marking off a point on, or parallel to, a diagonal line the data is multiplied by 0.707 and then marked off with the scale ( $\sin 45^\circ = 0.707$ ).

The  $\text{NaNO}_3$  field only is shown in Fig. 44, and this was plotted from Table 29 as follows:

From the  $\text{NaNO}_3$  corner 0.179 Cl was measured along the  $\text{NaNO}_3\text{.NaCl}$  edge of the prism to give the point  $A_2$ . In the same way 0.037  $\text{SO}_4$  gave the point  $I_2$ . The point  $A_3$  was found by measuring 0.17 Cl along the  $\text{NaNO}_3\text{.Cl}$  edge and then from the point obtained measuring 0.030  $\text{SO}_4$  towards  $\text{Na}_2\text{SO}_4$  and parallel to the  $\text{NaNO}_3\text{.Na}_2\text{SO}_4$  edge of the prism. That is, the point  $A_3$  was plotted in the triangle  $\text{NaNO}_3\text{.NaCl.Na}_2\text{SO}_4$ , which is one end of the prism. In a similar way, the point  $K_2$  was found by measuring 0.462 K from the  $\text{NaNO}_3$  corner along the  $\text{NaNO}_3\text{.KNO}_3$  edge. The point  $I_3$  was also similarly obtained by measuring 0.471 K along the same edge and by measuring 0.020  $\text{SO}_4$  from the point found towards the  $\text{SO}_4$  edge and parallel to the  $\text{NaNO}_3\text{.Na}_2\text{SO}_4$  edge of the prism. The point  $C_3$  was found by measuring 0.465 K along the  $\text{NaNO}_3\text{.KNO}_3$  edge and then, from the point found, measuring 0.080 Cl parallel to the  $\text{NaNO}_3\text{.NaCl}$  edge.

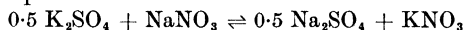
The remaining point,  $A_4$ , is an internal point and requires slightly different procedure: Cl and  $\text{SO}_4$  are measured first and finally K. From the  $\text{NaNO}_3$  corner measure 0.078 Cl along the  $\text{NaNO}_3\text{.NaCl}$  edge; from the point thus found measure 0.018  $\text{SO}_4$  parallel to the  $\text{NaNO}_3\text{.Na}_2\text{SO}_4$  edge, which fixes a point within the triangle  $\text{NaNO}_3\text{.NaCl.Na}_2\text{SO}_4$ . From this point measure 0.462 K parallel to the  $\text{NaNO}_3\text{.KNO}_3$  edge to find the point  $A_4$ .

The figure is now completed by drawing lines from  $I_2$  to  $A_3$ , from  $A_3$  to  $A_2$ , from  $I_2$  to  $I_3$ , from  $I_3$  to  $K_2$ , from  $K_2$  to  $C_3$  and from  $C_3$  to  $A_2$ . Finally, draw the radiating lines from  $A_4$  to  $A_3$ , to  $C_3$  and to  $I_3$ .

The figures 2, 3 and 4 following each letter denote the number of solid phases in equilibrium with the solution. Thus points on the edges of the prism are marked 2, points on the faces of the prism are marked 3 and internal points 4.

The completed figure is the  $\text{NaNO}_3$  field and should be compared with Figs. 41 and 42. The  $\text{KNO}_3$  field could conveniently be plotted on the same diagram; in fact, all the fields could be plotted on this diagram, but it might be convenient to make a new diagram for the sulphate and chloride fields arranging for the sulphate and chloride edge of the prism respectively, to be in the centre for more convenient plotting.

The lines bounding the  $\text{NaNO}_3$  field have been drawn as straight lines; actually they are curves, and where data is available intermediate points can be plotted and the shape of the curves shown. In practice it is found that many of the curves do approximate to straight lines, but there are exceptions. In Fig. 41 a dotted line is shown along one of the edges of the  $\text{Na}_2\text{SO}_4$  field. This dotted line is the curve separating the  $\text{Na}_2\text{SO}_4$  and glaserite fields in the reciprocal pair



with water at 75°C. This dotted line indicates that the surface separating the  $\text{Na}_2\text{SO}_4$  and glaserite fields in the prism does not actually approximate to a plane surface, but the fact is unimportant for a general study.

**Projection of the Quinary with Quantitative Examples.** Phase reactions within

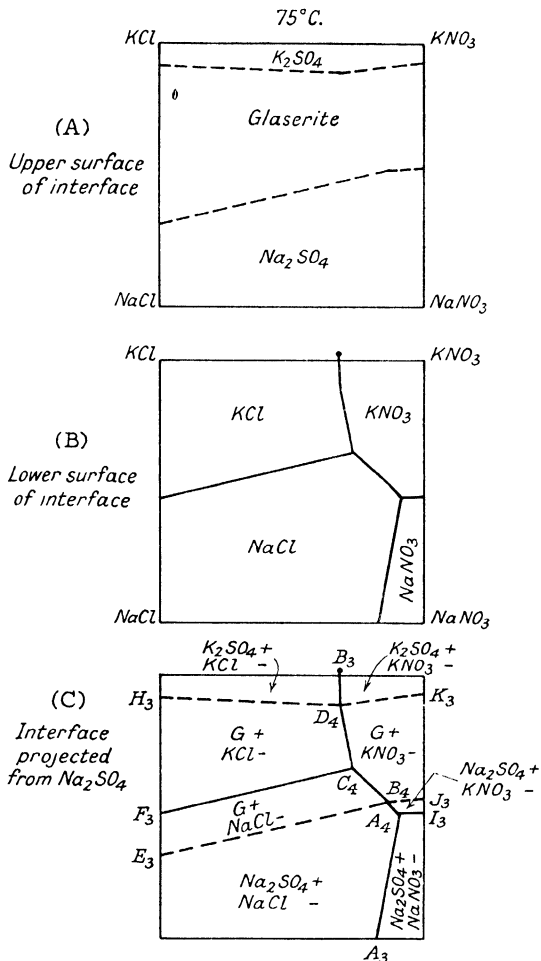


FIG. 45.

a quinary system could be followed on a space model made of wire, but the technique would be difficult and tedious. A projection similar to Fig. 41 or Fig. 44 could be used, but internal points could not be read on the diagram. An orthogonal projection on one of the square sides of the figure also has limitations.



In the case of the quaternary system, represented within a pyramid, the difficulty was overcome by using Jänecke's projection, that is, a projection on the base from the water

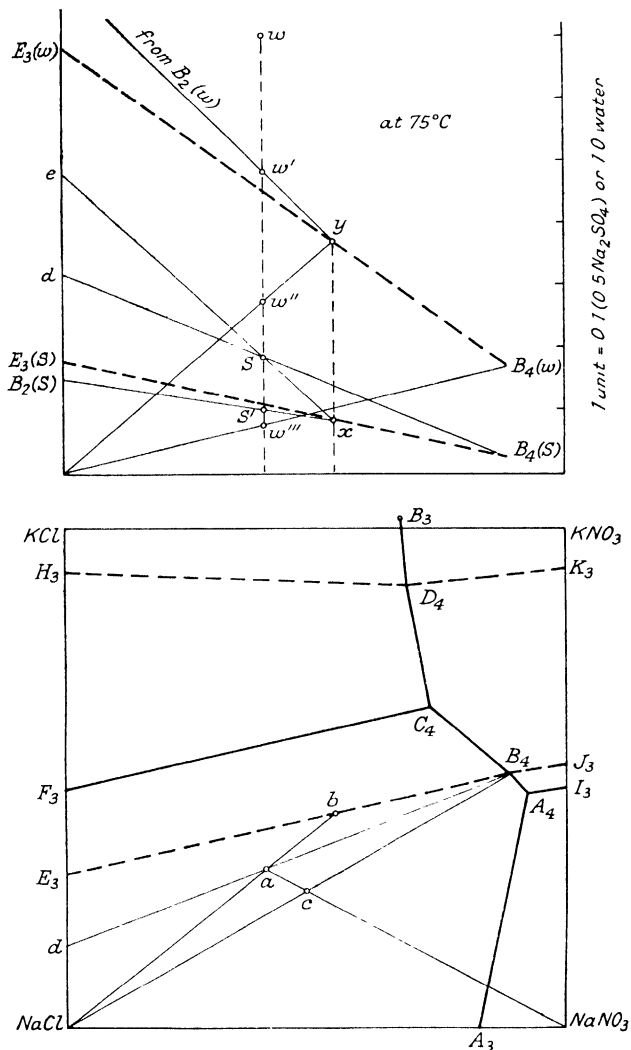


FIG. 46.

apex. The quinary system may be represented in a similar way. Water has already been eliminated and is not represented within the prism. One of the salts may now be eliminated by projecting from the corner, representing that salt, on to the square opposite. In this

case a square diagram is obtained as a Jänecke's type of projection of a square-based pyramid with the salt, to be eliminated, at the apex of projection. The pyramid is not a regular pyramid.

As an example, in the system represented by Fig. 41,  $\text{Na}_2\text{SO}_4$  may be eliminated by projecting from the  $\text{Na}_2\text{SO}_4$  corner on to the  $\text{KCl.KNO}_3.\text{NaNO}_3.\text{NaCl}$  square. It will readily be seen that only points within the pyramid  $\text{Na}_2\text{SO}_4.\text{KCl.KNO}_3.\text{NaNO}_3.\text{NaCl}$  will project on the square. Any other points within the prism would project on to the base beyond the line  $\text{KCl.KNO}_3$ ;  $\text{K}_2\text{SO}_4$  itself would project on the base at a point where the lines  $\text{NaCl.KCl}$  and  $\text{NaNO}_3.\text{KNO}_3$  meet at infinity.

Thus the choice of salt to be eliminated depends upon the part of the system to be studied. The salt must be chosen so that the required points and curves come within the pyramid of which that salt is the apex. If this is not convenient, it may be necessary to use two projections or to project some points outside the square.

For the example to be studied the projection has been taken from the  $\text{Na}_2\text{SO}_4$  corner of Fig. 41, and Fig. 45 is the projection. Fig. 45c shows the complete projection of the interface between the sulphates ( $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  and glaserite) and  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$  and  $\text{NaCl}$ . The diagram should be regarded as an open square with  $\text{KCl.KNO}_3$  as the open end.

The square diagram should be compared with Fig. 41 and, for greater clarity, with Fig. 42. The figure is a plan of the upper surface of the interface, that is, of lower surfaces of the  $\text{K}_2\text{SO}_4$ , glaserite and  $\text{Na}_2\text{SO}_4$  fields. This is made clear by Fig. 45a. It is also a plan of the lower surface of the interface, that is, of the upper surfaces of the four fields represented by the four corners. This is shown in Fig. 45b.

On the composite diagram, Fig. 45c, a convention is suggested for marking the areas to show what field is above, indicated as +, and what field is below, indicated as -. Comparison of Figs. 45A, B and C makes this clear.

A point on this diagram might represent a solution containing no sulphate, some sulphate or saturated as to sulphate, or with different amounts of sulphate in the solid phase.

The diagram of Fig. 45c has been repeated in Fig. 46, but an elevation has been introduced assuming that the two sides of the prism have been opened out so that the sulphate may be represented vertically above the base. The plan may then be considered as an orthogonal projection of the opened-out elevation. (This may be understood by comparison with Fig. 39.) The elevation gives the amount of sulphate (representing  $\text{Na}_2\text{SO}_4$ ), *in addition* to 1 mol of the other salts.

Water may also be represented vertically on the elevation and a solution, saturated as to *two salts*, would be represented by a point on the plan and by two points on the elevation, vertically above the point on the plan. One point on the elevation would lie on the sulphate saturation *surface* and the other on the water saturation *surface*. If the solution were saturated as to *three salts* the two points on the elevation would lie vertically above but on their respective *curves*.

For plotting the diagram of Fig. 46 the required data in Table 29 have been calculated to eliminate  $\text{Na}_2\text{SO}_4$ , that is, so that the other salts add up to 1 mol. The re-calculated data is given in Table 30 and the same reference letters have been used.

For the calculation, the mol fraction of  $\text{SO}_4$  is separated from the other negative ions. As  $\text{Na}_2\text{SO}_4$  is to be eliminated, the same mol fraction is subtracted from the total Na mol fraction. The total is then calculated back to unity by simple proportion. Two examples should make this clear.

TABLE 30

THE QUINARY SYSTEM,  $\text{Na.K.NO}_3.\text{Cl.Na}_2\text{SO}_4.\text{WATER}$  AT  $75^\circ \text{C.}$ Mols per Mol of Salts (less  $\text{Na}_2\text{SO}_4$ ).

The data from Table 29 have been calculated to represent a projection from the  $\text{Na}_2\text{SO}_4$  corner of the prism.

Ref.	Na.	K.	$\text{NO}_3$ .	Cl.	0.5 $\text{Na}_2\text{SO}_4$ .	Water.	Solid Phase.
$B_2$	1	—	—	1	0.148	7.98	$\text{Na}_2\text{SO}_4 + \text{NaCl}$
$I_2$	1	—	1	—	0.038	3.25	$\text{NaNO}_3 + \text{Na}_2\text{SO}_4$
$A_3$	1	—	0.825	0.175	0.031	3.25	$\text{NaNO}_3 + \text{Na}_2\text{SO}_4 + \text{NaCl}$
$B_3$	—0.013	1.013	0.674	0.326	0.013	3.39	$\text{KNO}_3 + \text{K}_2\text{SO}_4 + \text{KCl}$
$E_3$	0.694	0.306	—	1	0.176	6.78	$\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{G}$
$F_3$	0.526	0.474	—	1	0.053	6.34	$\text{NaCl} + \text{KCl} + \text{G}$
$H_3$	0.095	0.905	—	1	0.053	7.92	$\text{KCl} + \text{K}_2\text{SO}_4 + \text{G}$
$I_3$	0.519	0.481	1	—	0.024	1.49	$\text{NaNO}_3 + \text{KNO}_3 + \text{Na}_2\text{SO}_4$
$J_3$	0.477	0.523	1	—	0.029	1.74	$\text{Na}_2\text{SO}_4 + \text{KNO}_3 + \text{G}$
$K_3$	0.072	0.928	1	—	0.034	3.30	$\text{KNO}_3 + \text{K}_2\text{SO}_4 + \text{G}$
$A_4$	0.529	0.471	0.920	0.080	0.018	1.47	$\text{NaNO}_3 + \text{KNO}_3 + \text{NaCl} + \text{Na}_2\text{SO}_4$
$B_4$	0.492	0.508	0.884	0.116	0.025	1.70	$\text{KNO}_3 + \text{NaCl} + \text{Na}_2\text{SO}_4 + \text{G}$
$C_4$	0.359	0.641	0.727	0.273	0.017	2.31	$\text{KNO}_3 + \text{NaCl} + \text{KCl} + \text{G}$
$D_4$	0.118	0.882	0.684	0.316	0.017	3.10	$\text{KNO}_3 + \text{KCl} + \text{K}_2\text{SO}_4 + \text{G}$

G = Glaserite:  $3\text{K}_2\text{SO}_4.\text{Na}_2\text{SO}_4$ .

Solution  $B_4$  has the following composition:

	Na.	K.	$\text{NO}_3$ .	Cl.	0.5 $\text{SO}_4$ .
Deduct 0.024 Na.	0.504	0.496	0.863	0.113	0.024
	0.480	0.496	0.863	0.113	
Divide by $(1.0 - 0.024) = 0.976$	0.492	0.508	0.884	0.116	0.025 <sup>1</sup>

Solution  $E_3$  has the following composition:

	Na.	K.	$\text{NO}_3$ .	Cl.	0.5 $\text{SO}_4$ .
Deduct 0.150 Na	0.740	0.260	0.0	0.850	0.150
	0.590	0.260	0.0	0.850	
Divide by $(1.0 - 0.150) = 0.850$	0.694	0.306	0.0	1.0	0.176 <sup>1</sup>

The result of subtracting the mol fraction of Na equivalent to  $\text{SO}_4$  (half-mol) will always be positive if the complex under consideration comes within the relevant pyramid. If it comes outside the pyramid then the result will be a negative value for Na, which means that the point will be plotted outside the square, that is, above the  $\text{KCl.KNO}_3$  side. This is sometimes necessary where the investigation overlaps the area of projection.

The water figures need not be altered but may remain the same as in Table 29, but, in this case, it must be remembered that the water figure applies to one mol of total salts and not to one mol of salts without sulphate.

The data are plotted in terms of Na, K,  $\text{NO}_3$  and Cl on the square base plan, and the  $\text{SO}_4$  (representing  $\text{Na}_2\text{SO}_4$ ) and the water are plotted vertically on the elevation using any

<sup>1</sup> Now in terms of 0.5  $\text{Na}_2\text{SO}_4$ .

convenient scales. The composition of any point may be read on the diagram and may be calculated back to mols per mol of total salts. For example, take solution  $B_4$ .

$B_4$ is read from the diagram as . . .	Na.	K.	$\text{NO}_3$	Cl	$0.5 \text{ Na}_2\text{SO}_4$
Add 0.025 Na for $\text{Na}_2\text{SO}_4$ . . .	0.492	0.508	0.884	0.116	0.025
	0.025				
	0.517	0.508	0.884	0.116	0.025
Divide by 1.025 . . . . .	0.504	0.496	0.863	0.113	0.024 <sup>1</sup>

Phase reactions may be followed quantitatively on this type of diagram and at any stage the compositions of solution and solid phases, as read on the diagram, may be calculated to the compositions in terms of 1 mol of salts, and the correct proportion of each may be found by inspection, as will be seen later.

It is only necessary to plot the part of the diagram being studied and this especially applies to the elevation. In Fig. 46 the whole internal system at 75° C. has been plotted on the plan. The sulphate and water elevations of the curve  $E_3B_4$  only, have been plotted on the elevation; the water curve is marked  $E_3(w).B_4(w)$  and the sulphate curve is marked  $E_3(s).B_4(s)$ .

The point  $a$  on the plan has been taken to represent a complex, and the phase reactions on the removal of water from this complex will now be studied quantitatively. The composition of the complex *as represented on the diagram* is as follows:

Na . . . . .	0.680 mol
K . . . . .	0.320 „
$\text{NO}_3$ . . . . .	0.402 „
Cl . . . . .	0.598 „
0.5 $\text{Na}_2\text{SO}_4$ . . . . .	0.184 „
Water . . . . .	7.000 „

The composition in the more usual terms of 1 mol of total salts in complex  $a$  is:

Na . . . . .	0.730 mol
K . . . . .	0.270 „
$\text{NO}_3$ . . . . .	0.340 „
Cl . . . . .	0.505 „
0.5 $\text{SO}_4$ . . . . .	0.155 „
Water . . . . .	7.000 „

The point  $s$  represents the complex on the elevation from the point of view of  $\text{Na}_2\text{SO}_4$ , while the point  $w$  on the elevation represents water for the same complex. It is seen that the complex, represented by  $s$ , would lie above the NaCl field and within the  $\text{Na}_2\text{SO}_4$  field if the correct amount of water were present.<sup>2</sup> The position of  $w$  shows that the complex is unsaturated solution, and the quantitative example to be worked out is the removal of water from solution  $w$ .

ISOTHERMAL REMOVAL OF WATER. If sufficient water is removed from the solution  $w$ , a mixture of NaCl and  $\text{Na}_2\text{SO}_4$  will be deposited when the amount of water is such that

<sup>1</sup> Now as 0.5  $\text{SO}_4$ .

<sup>2</sup> The point  $s$  is within the  $\text{Na}_2\text{SO}_4$  field of the space diagram (the prism), but water had been eliminated to prepare that diagram. When water is re-introduced a four-dimensional diagram would result and the complex might then be in the  $\text{Na}_2\text{SO}_4$  field or in the field of all solution.

there are two solid phases. This is seen because the point  $a$  lies in the field marked  $(\text{Na}_2\text{SO}_4 +, \text{NaCl} -)$ . (See Fig. 45.) The  $\text{NaCl}$  corner of the square represents  $\text{NaCl}$  or  $\text{NaCl} + \text{Na}_2\text{SO}_4$ , and therefore a line drawn from this corner, through  $a$ , to meet the curve  $E_3B_4$  at  $b$  is the path of crystallization of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  on the surface dividing these two fields. This line is projected on to the elevation by plotting  $B_2$  (see Table 30 and compare Fig. 41) for sulphate and for water on the elevation, and drawing two lines  $B_2(s)$  to  $x$  and  $B_2(w)$  to  $y$ , where  $x$  and  $y$  are the points corresponding to  $b$  on the respective curves, and vertically above it.

The solution, as represented by the point  $s$ , is within the  $\text{Na}_2\text{SO}_4$  field (compare Fig. 46 with Fig. 45c). If sufficient water is removed it will become saturated and  $\text{Na}_2\text{SO}_4$  will be deposited. This will be when water is somewhere between  $w$  and  $w'$ , because  $w'$  represents a solution on the water saturation surface and saturated as to the two salts,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ . The vertical distance  $ww'$  indicates the amount of water to be removed from 1 mol of salts before both  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  will be deposited. The corresponding point on the sulphate saturation surface for the solution saturated as to  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  is  $s'$ . The distance  $ss'$  indicates the mols of  $\text{Na}_2\text{SO}_4$  deposited from 1 mol of the other salts in solution  $s$ . It should be noted that the composition of the salts in solution, as represented by the point  $s$ , does not alter until the water content has reached the position between  $w$  and  $w'$  at which  $\text{Na}_2\text{SO}_4$  begins to be deposited.

Having reached the composition represented by the points  $w'$  and  $s'$  (and being still at  $a$  on the plan), if more water is removed, the point, representing solution, will move from  $a$  on the plan towards  $b$ . On the elevation it will move from  $s'$  towards  $x$  and from  $w'$  towards  $y$ . A mixture of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  will be deposited.

When water has been removed to the point  $w''$  the composition of the solution will be represented by  $b$  on the plan, and by  $x$  for sulphate, and  $y$  for water on the elevation. The complex will, of course, still be at  $a$ . The composition of the solid phase will be at  $\text{NaCl}$  on the plan (representing  $\text{NaCl} + \text{Na}_2\text{SO}_4$ ) and at  $e$  on the elevation, and there will be  $b$  to  $a$  parts of solid and  $\text{NaCl}$  to  $a$  parts of solution. The solution  $b$  is saturated as to  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and glaserite, the glaserite phase having just appeared.

If the removal of water is still further continued the solution point will move from  $b$  along the curve towards  $B_4$ . On the elevation it moves from  $y$  towards  $B_4(w)$  and from  $x$  towards  $B_4(s)$ .  $\text{NaCl}$  and glaserite will be deposited while  $\text{Na}_2\text{SO}_4$  will be dissolved. (Compare incongruently saturated solutions in the quaternary system and Fig. 34a.) Any point on the curve  $E_3B_4$  is incongruently saturated and the point, representing the solution in question, can only remain on the curve as long as there is  $\text{Na}_2\text{SO}_4$  in the solid phase. If the solid phase were removed when the solution was at  $b$ , then the further removal of water would cause the solution point to leave the curve and cross the  $\text{NaCl}$ .glaserite surface towards the curve  $C_4B_4$ .

In the case being considered the  $\text{Na}_2\text{SO}_4$  is left in the solid phase and so the solution point follows the curve  $E_3B_4$ , reaching  $B_4$  when the water is such that it is represented by the point  $w''$  on the elevation. The composition of the solution  $B_4$  will also be represented by  $B_4(s)$  and  $B_4(w)$  on the elevation. The solid phase, a mixture of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and glaserite, may be read at  $d$  on the plan, in terms of  $\text{Cl}$ ,  $\text{Na}$  and  $\text{K}$ , and at  $d$  on the elevation in terms of  $\text{Na}_2\text{SO}_4$ ; thence it is calculated to 1 mol of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ , and may be further calculated to  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and glaserite. There will be  $B_4$  to  $a$  parts of solid and  $d$  to  $a$  parts of solution.

By the removal of water from complex  $a$ , the solution was enriched in potassium and

TABLE 31

REMOVAL OF WATER FROM COMPLEX *a* TO GIVE SOLUTION *b*

- METHOD :** (i) Read composition of complex, solution and solid phase on the diagram.  
(ii) Calculate to mols per mol of total salts.  
(iii) Read proportion of solution *b* to solid *e* on line NaCl to *b* on the diagram, using NO<sub>3</sub> as co-ordinate, and calculate to one mol of salts in complex *a*.  
(iv) Inspect composition (in terms of mols per mol of total salts) and read true proportion of solution *b* to solid *e* (0.540 *a* becomes 0.499*a*, 0.745*b* becomes 0.681 *b*, solid *e* is found by difference). Calculate to one mol of the salts in complex *a*.

Composition in terms of mols per mol of total salts

Composition read on diagram  
(= one mol without Na<sub>2</sub>SO<sub>4</sub>)

	Na.	K.	NO <sub>3</sub>	Cl.	0.5 Na <sub>2</sub> SO <sub>4</sub>	Water.
(i)						
1 mol complex <i>a</i>	0.680	0.320	0.402	0.598	0.184	7.0
1 mol solution <i>b</i>	0.570	0.430	0.540	0.460	0.083	3.7
1 mol solid <i>e</i>	1.0	—	—	1.0	0.478	—

	Na.	K.	NO <sub>3</sub>	Cl.	0.5 SO <sub>4</sub>	Water.
(ii)						
1 mol complex <i>a</i>	0.730	0.270	0.340	0.505	0.155	7.0
1 mol solution <i>b</i>	0.603	0.397	0.499	0.425	0.076	3.7
1 mol solid <i>e</i>	1.0	—	—	0.676	0.324	—

Read from diagram

- (iii) Complex *a* = solution *b* + solid *e*  
0.540      0.402      0.138  
1.0      0.745      0.255

By inspection of above data

- (iv) Complex *a* = solution *b* + solid *e*  
0.499      0.340      0.159  
1.0      0.681      0.319

Summary and check of balance to show that one mol of salts as complex *a* gives the correct proportions of solution *b* and solid *e* when (7.0 - 2.75) = 4.25 mols of water are removed.

Composition and proportion from diagram

	Na.	K.	NO <sub>3</sub>	Cl.	0.5 Na <sub>2</sub> SO <sub>4</sub>	Water.
0.745 mol <i>b</i>	0.425	0.320	0.402	0.343	0.062	2.75
0.255 mol <i>e</i>	0.255	—	—	0.255	0.122	—
Water removed	—	—	—	—	—	4.25
1.000 mol <i>a</i>	0.680	0.320	0.402	0.598	0.184	7.0

Re-adjusted composition and proportion

	Na.	K.	NO <sub>3</sub>	Cl.	0.5 SO <sub>4</sub>	Water.
0.681 mol <i>b</i>	0.411	0.270	0.340	0.289	0.052	2.75
0.319 mol <i>e</i>	0.319	—	—	0.216	0.103	—
Water removed	—	—	—	—	—	4.25
1.000 mol <i>a</i>	0.730	0.270	0.340	0.505	0.155	7.0

TABLE 32

REMOVAL OF WATER FROM COMPLEX  $a$  TO GIVE SOLUTION  $B_4$ 

## METHOD:

- (i) Read composition of complex, solution and solid phase on the diagram.  
 (ii) Calculate to mols per mol of total salts.  
 (iii) Read proportion of solution  $B_4$  to solid  $d$  on line  $d$  to  $B_4$  on the diagram, using  $\text{NO}_3$  as co-ordinate, and calculate to one mol of salts in complex  $a$ .  
 (iv) Inspect composition (in terms of mols per mol of total salts) and read true proportion of solution  $B_4$  to solid  $d$  (0.884  $a$  becomes 0.863  $a$ , 0.455  $B_4$  becomes 0.394  $B_4$ , solid  $d$  is found by difference). Calculate to one mol of the salts in complex  $a$ .

*Composition read on diagram*  
 (= one mol without  $\text{Na}_2\text{SO}_4$ )

	Na.	K.	$\text{NO}_3$	Cl.	$0.5 \text{ Na}_2\text{SO}_4$	Water.
(i) 1 mol complex $a$	0.680	0.320	0.402	0.598	0.184	7.0
1 mol solution $B_4$	0.492	0.508	0.884	0.116	0.025	1.7
1 mol solid $d$	0.837	0.163	—	1.0	0.318	—

*Read from diagram*

- (iii) Complex  $a$  = solution  $B_4$  + solid  $d$   
 0.884  
 1.0      0.455      0.545

*Summary and check of balance* to show that one mol of salts as complex  $a$  gives the correct proportions of solution  $B_4$  and solid  $d$  when (7.0 - 0.78) = 6.22 mols of water are removed.

*Composition and proportion from diagram*

	Na.	K.	$\text{NO}_3$	Cl.	$0.5 \text{ Na}_2\text{SO}_4$	Water.
0.455 mol $B_4$	0.224	0.231	0.402	0.053	0.011	0.78
0.545 mol $d$	0.456	0.089	—	0.545	0.173	—
Water removed	—	—	—	—	—	6.22
1.000 mol $a$	0.680	0.320	0.402	0.598	0.184	7.0

*Composition in terms of mols per mol of total salts*

	Na.	K.	$\text{NO}_3$	Cl.	$0.5 \text{ SO}_4$	Water.
1 mol complex $a$	0.730	0.270	0.340	0.505	0.155	7.0
1 mol solution $B_4$	0.504	0.496	0.863	0.113	0.024	1.7
1 mol solid $d$	0.876	0.124	—	0.759	0.241	—

*By inspection of above data*

- (iv) Complex  $a$  = solution  $B_4$  + solid  $d$   
 0.863  
 1.0      0.394      0.606

*Summary and check of balance* to show that one mol of salts as complex  $a$  gives the correct proportions of solution  $B_4$  and solid  $d$  when (7.0 - 0.78) = 6.22 mols of water are removed.

*Re-adjusted composition and proportion*

	Na.	K.	$\text{NO}_3$	Cl.	$0.5 \text{ SO}_4$	Water.
0.394 mol $B_4$	0.198	0.196	0.340	0.045	0.009	0.78
0.606 mol $d$	0.532	0.074	—	0.460	0.146	—
Water removed	—	—	—	—	—	6.22
1.000 mol $a$	0.730	0.270	0.340	0.505	0.155	7.0

greatly enriched in nitrate, but some of the potassium was lost in the solid phase. If the object had been to recover the potassium, then  $\text{NaNO}_3$  could have been added to the original solution to move it to the point  $c$  on the plan. Then the removal of water would have caused the composition of the solution to move directly to  $B_4$  with a solid phase of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  only.

Tables 31 and 32 show quantitatively how the isothermal removal of water from 1 mol of complex  $a$  gives solution  $b$  and then solution  $B_4$ , with the proportion and actual quantities and composition of solution and solid phases. The following explanation should make the method clear.

The compositions as read on the diagram (plan and elevation) are the correct compositions, but they are not in a familiar form. Part of the sodium is read as  $\text{Na}$  ion on the plan and part of it is read as  $\text{Na}_2\text{SO}_4$  on the elevation. The total, including  $\text{Na}_2\text{SO}_4$ , is more than 1 mol of salts, but may be calculated to represent 1 mol.

The proportions of solution to solid, as read on the plan, are distorted because the amount of  $\text{Na}_2\text{SO}_4$  varies on different parts of the diagram, i.e. on the projection of the interface. A line drawn from the point representing the solution to the point, representing the solid phase, and passing through the complex represents the amount of complex. On Fig. 47 this line is  $b$  to  $\text{NaCl}$  and measures 0.540 mol using the base of the square for measurement. This can, therefore, be taken as 0.540 mol of complex  $a$ , which is the same as the  $\text{NO}_3$  content of 1 mol of solution  $b$ . In the same way the amount of solution  $b$  is the same as the  $\text{NO}_3$  content of 1 mol of complex  $a$ , i.e.  $\text{NaCl}$  to  $a$ . The expression 1 mol of complex  $a$  here ignores the water content and means a complex with salt content, less  $\text{Na}_2\text{SO}_4$ , of 1 mol. The corrected proportions may be found by inspection of the data read from the diagram after it has been adjusted to represent 1 mol of *total* salts, including  $\text{Na}_2\text{SO}_4$ .

For example, 0.540 mol of complex  $a$  (line  $b$  to  $\text{NaCl}$ , and  $\text{NO}_3$  content of 1 mol of solution  $b$  as read on the diagram) becomes 0.499 mol of complex  $a$  ( $\text{NO}_3$  content of solution  $b$  as mols per mol of total salts). The same final result would be obtained if the line  $b$  to  $\text{NaCl}$  were measured parallel to the vertical sides of the square: in this case,  $\text{K}$  would be taken instead of  $\text{NO}_3$ .

**COOLING.** Having followed some reactions on a quinary isotherm it is now proposed to consider a case of cooling a solution.

Table 33 gives the data for plotting the same quinary but at  $25^\circ\text{C}$ . The same letters, but small case, have been used when the solutions have the same solid phases. A diagram like Fig. 41 should be plotted by the reader for comparison, when it will be noted that the figure obtained is similar to Fig. 41, but that the  $\text{Na}_2\text{SO}_4$  field (see Fig. 45A) has become two fields:  $\text{Na}_2\text{SO}_4$  on the  $\text{NaCl}$  side and darapskite on the  $\text{NaNO}_3$  side. In addition to this, there is a field for  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  above the  $\text{Na}_2\text{SO}_4$  and darapskite fields (not shown in Fig. 47). The projection from the  $\text{Na}_2\text{SO}_4$  corner of the prism is shown in Fig. 47 and was plotted from the data in Table 34. The point  $A_4$  at  $75^\circ\text{C}$ . has become  $e_4$  at  $25^\circ\text{C}$ ., saturated as to  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{NaCl}$  and darapskite. The curve  $A_4I_3$  of Fig. 46 has become  $e_4m_3$ , representing solution saturated as to  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and darapskite and containing some chloride. The sulphate and water elevations of the curve  $e_4m_3$  have been included in Fig. 47, and the point  $A_4$  from Table 30 ( $75^\circ\text{C}$ .) has been plotted on plan and elevation because it is proposed to study the effect of cooling this solution from  $75^\circ\text{C}$ . to  $25^\circ\text{C}$ .

Solution  $A_4$  might have been obtained by adding the required amount of  $\text{NaNO}_3$  to the complex  $a$  already studied on Fig. 46 and removing the correct amount of water.

It is proposed to consider two examples of cooling the solution. In the first example



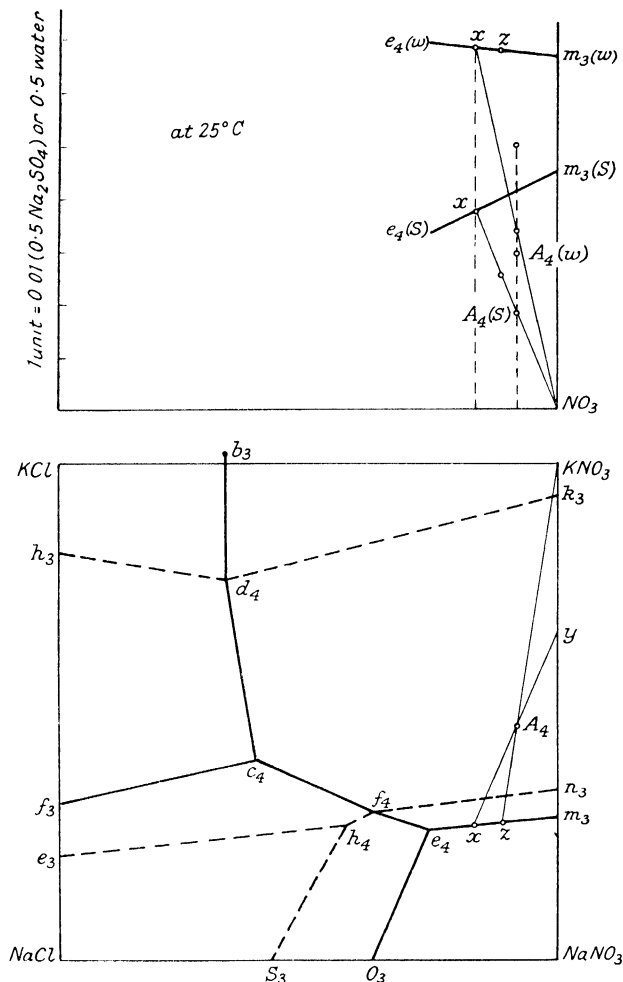


FIG. 47.

the solution will be diluted with a small amount of water and a mixture of  $NaNO_3$  and  $KNO_3$  obtained as solid phase. In the second example the solution will be diluted with a larger amount of water and pure  $KNO_3$  obtained as solid phase when cooled to 25°C.

*First Example.* On the plan the point  $A_4$  appears in the  $KNO_3$  or the glaserite fields at 25°C. (Compare Fig. 45A and B.) On the elevation  $A_4(s)$  is below the  $KNO_3$ -glaserite interface which means that, within the prism, the point  $A_4$  is inside the three-dimensional field of  $KNO_3$ .

TABLE 33

THE QUINARY SYSTEM: SODIUM, POTASSIUM, SULPHATE, NITRATE, CHLORIDE, WATER, AT 25° C.  
Mols per Mol of Total Salts.

(Adapted from data by Blasdale, 1918, Reinders, 1915, and Cornec, Krombach and Spack, 1929-30).

Ref.	Na	K.	0.5 SO <sub>4</sub>	NO <sub>3</sub>	Cl	Water.	Solid Phase.
<i>a</i> <sub>1</sub>	1	—	—	1	—	5.14	NaNO <sub>3</sub>
<i>b</i> <sub>1</sub>	1	—	—	—	1	9.12	NaCl
<i>c</i> <sub>1</sub>	1	—	1	—	—	13.20	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O
<i>d</i> <sub>1</sub>	—	1	1	—	—	40.20	K <sub>2</sub> SO <sub>4</sub>
<i>e</i> <sub>1</sub>	—	1	—	—	1	11.25	KCl
<i>f</i> <sub>1</sub>	—	1	—	1	—	14.65	KNO <sub>3</sub>
<i>a</i> <sub>2</sub>	1	—	—	0.624	0.376	5.02	NaNO <sub>3</sub> + NaCl
<i>b</i> <sub>2</sub>	1	—	0.205	—	0.795	8.00	Na <sub>2</sub> SO <sub>4</sub> + NaCl
<i>c</i> <sub>2</sub>	0.804	0.196	1	—	—	10.25	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O + G
<i>d</i> <sub>2</sub>	0.383	0.617	1	—	—	22.60	K <sub>2</sub> SO <sub>4</sub> + G
<i>e</i> <sub>2</sub>	—	1	0.036	—	0.964	10.90	K <sub>2</sub> SO <sub>4</sub> + KCl
<i>f</i> <sub>2</sub>	—	1	—	0.330	0.670	8.01	KNO <sub>3</sub> + KCl
<i>h</i> <sub>2</sub>	—	1	0.161	0.839	—	13.19	KNO <sub>3</sub> + K <sub>2</sub> SO <sub>4</sub>
<i>j</i> <sub>2</sub>	0.697	0.303	—	—	1	7.63	NaCl + KCl
<i>k</i> <sub>2</sub>	0.716	0.284	—	1	—	3.40	NaNO <sub>3</sub> + KNO <sub>3</sub>
<i>l</i> <sub>2</sub>	1	—	0.414	0.586	—	6.74	Na <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O
<i>m</i> <sub>2</sub>	1	—	0.075	0.925	—	5.00	NaNO <sub>3</sub> + D
<i>n</i> <sub>2</sub>	1	—	0.486	—	0.514	8.86	Na <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O
<i>o</i> <sub>2</sub>	1	—	0.374	0.626	—	6.59	Na <sub>2</sub> SO <sub>4</sub> + D
<i>b</i> <sub>3</sub>	—	1	0.022	0.325	0.653	7.90	KNO <sub>3</sub> + K <sub>2</sub> SO <sub>4</sub> + KCl
<i>c</i> <sub>3</sub>	0.740	0.260	—	0.740	0.260	3.54	NaNO <sub>3</sub> + KNO <sub>3</sub> + NaCl
<i>d</i> <sub>3</sub>	0.640	0.360	—	0.360	0.640	5.01	KNO <sub>3</sub> + NaCl + KCl
<i>e</i> <sub>3</sub>	0.832	0.168	0.210	—	0.790	7.36	Na <sub>2</sub> SO <sub>4</sub> + NaCl + G
<i>f</i> <sub>3</sub>	0.705	0.295	0.066	—	0.934	7.45	NaCl + KCl + G
<i>h</i> <sub>3</sub>	0.216	0.784	0.049	—	0.951	10.37	KCl + K <sub>2</sub> SO <sub>4</sub> + G
<i>k</i> <sub>3</sub>	0.259	0.741	0.211	0.789	—	10.21	KNO <sub>3</sub> + K <sub>2</sub> SO <sub>4</sub> + G
<i>l</i> <sub>3</sub>	0.869	0.131	0.489	—	0.380	8.66	Na <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O + G
<i>m</i> <sub>3</sub>	0.724	0.276	0.043	0.957	—	3.35	NaNO <sub>3</sub> + KNO <sub>3</sub> + D
<i>n</i> <sub>3</sub>	0.701	0.299	0.130	0.870	—	4.11	KNO <sub>3</sub> + D + G
<i>o</i> <sub>3</sub>	1	—	0.044	0.601	0.355	4.90	NaNO <sub>3</sub> + NaCl + D
<i>p</i> <sub>3</sub>	0.776	0.224	0.254	0.746	—	4.99	Na <sub>2</sub> SO <sub>4</sub> + D + G
<i>q</i> <sub>3</sub>	0.840	0.160	0.501	0.499	—	6.24	Na <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O + G
<i>s</i> <sub>3</sub>	1	—	0.112	0.381	0.507	6.00	Na <sub>2</sub> SO <sub>4</sub> + NaCl + D
<i>c</i> <sub>4</sub>	0.614	0.386	0.035	0.380	0.585	4.97	KNO <sub>3</sub> + NaCl + KCl + G
<i>d</i> <sub>4</sub>	0.263	0.737	0.037	0.321	0.642	7.00	KNO <sub>3</sub> + KCl + K <sub>2</sub> SO <sub>4</sub> + G
<i>e</i> <sub>4</sub>	0.750	0.250	0.032	0.719	0.249	3.49	NaNO <sub>3</sub> + KNO <sub>3</sub> + NaCl + D
<i>f</i> <sub>4</sub>	0.725	0.275	0.065	0.589	0.346	4.06	NaCl + KNO <sub>3</sub> + D + G
<i>h</i> <sub>4</sub>	0.755	0.245	0.084	0.527	0.389	4.42	NaCl + Na <sub>2</sub> SO <sub>4</sub> + D + G

D = Darapskite : NaNO<sub>3</sub> · Na<sub>2</sub>SO<sub>4</sub> · H<sub>2</sub>O.

G = Glaserite : 3K<sub>2</sub>SO<sub>4</sub> · Na<sub>2</sub>SO<sub>4</sub>.

When water is represented, solution *A*<sub>4</sub> at 25° C. can be in the KNO<sub>3</sub> field, the NaNO<sub>3</sub> + KNO<sub>3</sub> field, or the field of NaNO<sub>3</sub> + KNO<sub>3</sub> + darapskite, according to the amount of water present.

When the quaternary system was studied it will be remembered that a point on Jänecke's projection of the pyramid was within the field of one salt, two salts or three salts, according to the amount of water present (see Figs. 29, 30, and 31). It will be seen shortly that the point *A*<sub>4</sub> is in the field of three salts when the amount of water is as given in Table 29.

TABLE 34

THE QUINARY SYSTEM:  $\text{Na.K.NO}_3.\text{Cl.Na}_2\text{SO}_4.\text{WATER}$  AT  $25^\circ\text{C}$ .Mols per Mol of Salts (less  $\text{Na}_2\text{SO}_4$ ).

The data from Table 33 have been calculated to represent a projection from the  $\text{Na}_2\text{SO}_4$  corner of the prism.

Ref.	Na.	K	$\text{NO}_3$ .	Cl.	0.5 $\text{Na}_2\text{SO}_4$ .	Water.	Solid Phase.
$b_2$	1	—	—	1	0.258	8.00	$\text{Na}_2\text{SO}_4 + \text{NaCl}$
$m_2$	1	—	1	—	0.081	5.00	$\text{NaNO}_3 + \text{D}$
$b_3$	—0.020	1.020	0.332	0.668	0.022	7.90	$\text{KNO}_3 + \text{K}_2\text{SO}_4 + \text{KCl}$
$c_3$	0.787	0.213	—	1	0.266	7.36	$\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{G}$
$f_3$	0.684	0.316	—	1	0.071	7.45	$\text{NaCl} + \text{KCl} + \text{G}$
$h_3$	0.176	0.824	—	1	0.059	10.37	$\text{KCl} + \text{K}_2\text{SO}_4 + \text{G}$
$k_3$	0.061	0.939	1	—	0.267	10.21	$\text{KNO}_3 + \text{K}_2\text{SO}_4 + \text{G}$
$m_3$	0.711	0.289	1	—	0.045	3.35	$\text{NaNO}_3 + \text{KNO}_3 + \text{D}$
$n_3$	0.656	0.344	1	—	0.150	4.11	$\text{KNO}_3 + \text{D} + \text{G}$
$o_3$	1	—	0.629	0.371	0.046	4.90	$\text{NaNO}_3 + \text{NaCl} + \text{D}$
$s_3$	1	—	0.429	0.571	0.126	6.00	$\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{D}$
$c_4$	0.600	0.400	0.394	0.606	0.036	4.97	$\text{KNO}_3 + \text{NaCl} + \text{KCl} + \text{G}$
$d_4$	0.235	0.765	0.333	0.667	0.038	7.00	$\text{KNO}_3 + \text{KCl} + \text{K}_2\text{SO}_4 + \text{G}$
$e_4$	0.742	0.258	0.743	0.257	0.033	3.49	$\text{NaNO}_3 + \text{KNO}_3 + \text{NaCl} + \text{D}$
$f_4$	0.706	0.294	0.630	0.370	0.070	4.06	$\text{NaCl} + \text{KNO}_3 + \text{D} + \text{G}$
$h_4$	0.732	0.268	0.575	0.425	0.092	4.42	$\text{NaCl} + \text{Na}_2\text{SO}_4 + \text{D} + \text{G}$

D = Darapskite :  $\text{NaNO}_3.\text{Na}_2\text{SO}_4.\text{H}_2\text{O}$ .G = Glaserite :  $3\text{K}_2\text{SO}_4.\text{Na}_2\text{SO}_4$ .

On Fig. 47 a line is drawn from the  $\text{NO}_3$  corner (representing  $\text{NaNO}_3$  and  $\text{KNO}_3$  as solid phase) of the elevation through  $A_4(s)$  to meet the sulphate curve at  $x$ . The point  $x$  is then projected on to the water curve and on to the curve  $e_4m_3$  on the plan; these three points are marked  $x$  on the diagram and represent the solution required if the solid phase is to be free from darapskite with a maximum yield of  $\text{NaNO}_3$  and  $\text{KNO}_3$ .

Another line is drawn from the  $\text{NO}_3$  corner of the elevation to meet the water curve at  $x$ , and it will be noticed that this line does not pass through  $A_4(w)$  but passes above it at a point representing more water. This amount of water, represented by the vertical distance above  $A_4(w)$ , must be added to 1 mol of salts as solution  $A_4$  before the solution is cooled.

A line is drawn from  $x$  on the plan, through  $A_4$  to meet the nitrate side of the square at  $y$  which represents the composition of the solid phase.

The above reactions are followed quantitatively on Table 35.

It has been shown above that solution  $A_4$  needs dilution if the solid phase is to be  $\text{NaNO}_3$  and  $\text{KNO}_3$ , that is, the undiluted solution  $A_4$  at  $25^\circ\text{C}$ . was within the field of three salts,  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and darapskite.

If solution  $A_4$  had been cooled to  $25^\circ\text{C}$ . without dilution the solid phase would have been these same three salts. The solution at  $25^\circ\text{C}$ . would still have been represented on the curve  $e_4m_3$  at a point near  $x$ . The solid phase would have been represented near  $y$  on the plan and by two points on the  $\text{NO}_3$  vertical of the elevation representing  $\text{Na}_2\text{SO}_4$  (to be calculated to darapskite) and water of crystallization.

TABLE 35

COOLING SOLUTION  $A_4$  FROM 75° C. TO 25° C. TO OBTAIN A MIXTURE OF  $\text{NaNO}_3$  AND  $\text{KNO}_3$ 

- METHOD :** (i) Read composition of solution  $A_4$ , amount of water to be added, composition of solution  $x$  and solid  $y$  on the diagram.  
(ii) Calculate to mols per mol of total salts.  
(iii) Read proportion of solution  $x$  to solid  $y$  on line  $xy$  on the diagram, using Cl as co-ordinate and calculate to one mol of salts in solution  $A_4$ .  
(iv) Inspect composition (in terms of mols per mol of total salts) and read true proportion of solution  $x$  to solid  $y$  (0.165  $A_4$  becomes 0.159  $A_4$ , 0.080  $x$  becomes 0.078  $x$ , solid  $y$  is found by difference). Calculate to one mol of salts in solution  $A_4$ .

*Composition in terms of mols per mol of total salts.**Composition read on diagram  
(= one mol without  $\text{Na}_2\text{SO}_4$ )*

	Na.	K.	$\text{NO}_3$ .	Cl.	$\text{Na}_2\text{SO}_4$ .	Water.
1 mol solution $A_4$ Add 0.20 water	0.529	0.471	0.920	0.080	0.018	1.47 0.20
1 mol $A_4$ diluted	0.529	0.471	0.920	0.080	0.018	1.67
1 mol solution $x$	0.730	0.270	0.835	0.165	0.037	3.44
1 mol solid $y$	0.340	0.660	1.0	—	—	—

(i)

	Na.	K.	$\text{NO}_3$ .	Cl.	$\text{Na}_2\text{SO}_4$ .	Water.
1 mol solution $A_4$ Add 0.20 water	0.537	0.463	0.904	0.078	0.018	1.47 0.20
1 mol $A_4$ diluted	0.537	0.463	0.904	0.078	0.018	1.67
1 mol solution $x$	0.739	0.261	0.805	0.159	0.036	3.44
1 mol solid $y$	0.340	0.660	1.0	—	—	—

(ii)

*Read from diagram*

- (iii) Solution  $A_4$  = solution  $x$  + solid  $y$   
0.165 0.080  
1.0 0.485 0.515

*By inspection of above data*

- (iv) Solution  $A_4$  = solution  $x$  + solid  $y$   
0.159 0.078 0.081  
1.0 0.490 0.510

**SUMMARY AND CHECK OF BALANCE** to show that one mol of salts as solution  $A_4$  gives the correct proportion of solution  $x$  and solid  $y$ .  
*Re-adjusted composition and proportion.*

	Na.	K.	$\text{NO}_3$ .	Cl.	$\text{Na}_2\text{SO}_4$ .	Water.
0.485 mol $x$ 0.515 mol $y$	0.354 0.175	0.131 0.340	0.405 0.515	0.080 —	0.018 —	1.67 —
1.0 mol $A_4$ diluted	0.529	0.471	0.920	0.080	0.018	1.67

	Na.	K.	$\text{NO}_3$ .	Cl.	$\text{Na}_2\text{SO}_4$ .	Water.
0.490 mol $x$ 0.510 mol $y$	0.362 0.175	0.128 0.335	0.394 0.510	0.078 —	0.018 —	1.67 —
1.0 mol $A_4$ diluted	0.537	0.463	0.904	0.078	0.018	1.67

*Second Example.* If the right amount of water is added to solution  $A_4$  before cooling, the solid phase will be  $\text{KNO}_3$ , because the complex will have been moved into the field of one salt,  $\text{KNO}_3$ .

Draw a line on the plan from  $\text{KNO}_3$  through  $A_4$  to meet the curve  $e_4m_3$  at  $z$ . Project  $z$  on to the curve  $e_4m_3(w)$  on the elevation and draw a line from this point (not shown in the figure) to the  $\text{NO}_3$  corner. This line will cut the vertical line which passes through  $A_4(w)$  at a point above  $A_4(w)$ , giving the amount of water to be added to 1 mol of total salts as solution  $A_4$ .

When this diluted solution is cooled to  $25^\circ\text{C}$ ,  $\text{KNO}_3$  will be the solid phase. The composition of the solution at  $25^\circ\text{C}$ . will be represented by  $z$  on the plan and by the projection of  $z$  on the curve  $e_4m_3(w)$  on the elevation.

The sulphate in the solution will not be represented on the curve  $e_4m_3(s)$ . A line drawn from the  $\text{NO}_3$  corner of the elevation through  $A_4(s)$  is below the sulphate elevation of the curve. The sulphate in the solution at  $25^\circ\text{C}$ . is therefore represented by a point vertically below the projection of  $z$  and on the interface between the  $\text{KNO}_3$  and  $\text{NaNO}_3$  fields. Thus the cooled solution is saturated as to  $\text{KNO}_3$  ( $\text{KNO}_3$  is the solid phase), just saturated as to  $\text{NaNO}_3$  (it lies on the saturation surface) and is not saturated as to  $\text{Na}_2\text{SO}_4$ . The point representing the  $\text{Na}_2\text{SO}_4$  in the solution may be found on the elevation where the line from the  $\text{NO}_3$  corner and through  $A_4(s)$  would cut a vertical line through  $z$ .

In the above examples of cooling solution  $A_4$  it will have been noticed that the paths of crystallization from  $\text{KNO}_3$  and from a mixture of  $\text{NaNO}_3$  and  $\text{KNO}_3$  were drawn on the plan across the curve  $f_4n_3$  to meet the curve  $e_4m_3$ . These paths of crystallization cannot meet the curve  $f_4n_3$ , they pass below it and only appear to meet it on the plan.

It has been shown that when solution  $A_4$  is cooled to  $25^\circ\text{C}$ . without any added water, the solid phase is  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and darapskite. The solution, therefore, must be represented on the curve  $e_4m_3$ . When solution  $A_4$  is diluted before cooling, the composition of the solution at  $25^\circ\text{C}$ . must therefore be still further removed from the curve  $f_4n_3$ .

**General Notes on the Quinary System.** Assuming that there is no vapour phase and that pressure is fixed at one atmosphere, then, according to the phase rule when there are five phases of four solids and a solution, the quinary system will have one degree of freedom.

$$F = C - P + 1 \text{ (see next chapter).}$$

Number of components  $C = 5$ , number of phase  $P = 5$ . Therefore  $F = 5 - 5 + 1 = 1$ .

Temperature may, therefore, be selected when there are four solid phases as well as a solution.

If there are five solids as well as a solution, then there is no degree of freedom left and the temperature is that fixed by nature. There are several such cases in the system which has just been considered, but only one need be mentioned. The point  $A_4$  on Fig. 44 represents a solution saturated as to  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{KNO}_3$ , and is an isothermal invariant point at  $75^\circ\text{C}$ .

If the temperature is lowered, assuming the system remains at equilibrium, the point  $A_4$  moves nearer to  $\text{Na}$ ,  $\text{Cl}$  and  $\text{SO}_4$ , but the general shape of the  $\text{NaNO}_3$  field remains the same. At  $74^\circ\text{C}$ . a field of the double salt, darapskite, begins to form at the  $I_2$  corner as a small triangle on the  $\text{Na}_2\text{SO}_4$  surface  $I_2I_3A_4A_3$ . As the temperature is still further lowered the darapskite field grows until one of its surfaces covers the  $\text{Na}_2\text{SO}_4$  surface of the  $\text{NaNO}_3$  field completely, the last part to be covered being the  $A_4$  corner. At a little below  $55^\circ\text{C}$ . the  $\text{Na}_2\text{SO}_4$  surface has disappeared from the  $\text{NaNO}_3$  field and is replaced by darapskite,

and the point  $A_4$  has become, say,  $L_4$ , which represents a solution saturated as to  $\text{NaNO}_3$ ,  $\text{NaCl}$ , darapskite and  $\text{KNO}_3$ . At a definite temperature,  $55^\circ\text{C}$ ., there is a point, say  $M_5$ , which is saturated as to  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , darapskite and  $\text{KNO}_3$ .

If the system was at this required temperature and equilibrium was established, all five phases would be present and the point  $M_5$  on a diagram would be in contact with all five three-dimensional fields.

If heat is given to the system and equilibrium maintained, the phase reactions will be such as to absorb heat. (Principle of Le Chatelier.) Darapskite will be decomposed into  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$  and water, but the temperature and the composition of the solution will remain unchanged;  $\text{NaNO}_3$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  will dissolve as the darapskite is decomposed. When all the darapskite is decomposed this field is no longer in contact with the point  $M_5$ , a phase is lost and a degree of freedom gained. The temperature can now rise and a temperature may be selected. The solution will then be similar to  $A_4$ , saturated as to  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{KNO}_3$ .

If, on the other hand, heat had been removed from the system, the phase reactions would have been such as to give out heat. Darapskite would have been deposited and  $\text{Na}_2\text{SO}_4$  would have dissolved. The temperature and the composition of the solution would still have remained unchanged. In this case when the  $\text{Na}_2\text{SO}_4$  is all dissolved a degree of freedom is gained, and the temperature can fall and a temperature may be selected. When the system is at equilibrium the solution, similar to  $L_4$ , is saturated as to  $\text{NaNO}_3$ ,  $\text{NaCl}$ , darapskite and  $\text{KNO}_3$ .

To summarize :

Three solutions are being considered :

$A_4$  is saturated as to  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{KNO}_3$ .

$L_4$  is saturated as to  $\text{NaNO}_3$ ,  $\text{NaCl}$ , darapskite and  $\text{KNO}_3$ .

$M_5$  is saturated as to  $\text{NaNO}_3$ ,  $\text{NaCl}$ , darapskite,  $\text{Na}_2\text{SO}_4$  and  $\text{KNO}_3$ .

Solution  $M_5$  can exist, in contact with five solid phases only at a temperature fixed by nature. This temperature is  $55^\circ\text{C}$ .

Above this temperature the phase darapskite disappears and the solution becomes similar to  $A_4$ , its composition depending on the temperature selected.

Below this temperature the phase  $\text{Na}_2\text{SO}_4$  disappears and the solution becomes similar to  $L_4$ , its composition depending on the temperature.

The solution  $M_5$ , saturated as to, and in contact with, its five solid phases, represents a system invariant point; it has no degree of freedom in the condensed system. The composition of the solution is fixed by nature and the temperature also, which may not be altered if equilibrium is to be maintained. The temperature could easily be altered by applying sufficient heat quickly, but the system would no longer be in equilibrium; when equilibrium was re-established a phase would have disappeared.

There are six points representing solutions saturated as to five solid phases in the system  $\text{Na}$ ,  $\text{K}$ ,  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{Cl}$  and water between the temperatures of  $55^\circ\text{C}$ . and  $1.3^\circ\text{C}$ . Two of these points are caused by the disappearance of a phase from the whole system. At  $11.6^\circ\text{C}$ .,  $\text{Na}_2\text{SO}_4$  disappears and is replaced by Glauber's salt. The Glauber salt field touches the  $\text{NaCl}$  field on the  $\text{NaCl}$ — $\text{Na}_2\text{SO}_4$  edge of the diagram at  $17.9^\circ\text{C}$ ., and as the temperature falls it spreads over the  $\text{NaCl}$  field, displacing the  $\text{Na}_2\text{SO}_4$  surface. A little above the temperature of  $11.6^\circ\text{C}$ . the  $\text{Na}_2\text{SO}_4$  field is a small tetrahedron with its base on the three-dimensional  $\text{NaCl}$  field and its apex at the  $\text{Na}_2\text{SO}_4$  corner of the diagram.

As the temperature falls the tetrahedron shrinks and at  $11.6^{\circ}\text{C}$ . it vanishes, leaving a point on the NaCl field representing a solution saturated as to NaCl, glaserite, darapskite,  $\text{Na}_2\text{SO}_4$  and Glauber's salt. In a similar manner darapskite disappears at  $3.4^{\circ}\text{C}$ . A point representing a solution saturated as to five solid phases can be formed in another way, that is, like the case already described at  $55^{\circ}\text{C}$ . In this example the point occurs at the separation of two solid phases which have been in contact and the bringing into contact of two other solid phases which had been apart. In this example, above  $55^{\circ}\text{C}$ .,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  were in contact and below  $55^{\circ}\text{C}$ .,  $\text{KNO}_3$  and darapskite were in contact. There are in all four examples of this class between the temperatures mentioned, namely at  $55^{\circ}\text{C}$ .,  $38^{\circ}\text{C}$ .,  $8.7^{\circ}\text{C}$ . and  $1.3^{\circ}\text{C}$ .

The necessary data for plotting isotherms over the temperature range, mentioned in the preceding paragraph, can be found in *Caliche*, July and August, 1930 (Cornec, Krombach and Spack).

This concludes the practical examination of phase diagrams which this book set out to present. It does not claim to be in any way exhaustive, but it is suggested that sufficient examples have been given to enable the reader to tackle any phase problem of aqueous solutions which he is likely to meet. The methods of solving the more complicated cases may be legion, but they all follow the principles which have been illustrated. The next chapter is brief and is an attempt to give the reader a clear picture of just sufficient phase theory to help him to have a theoretical background to his more practical diagrams.

## CHAPTER XIII

### GIBBS'S PHASE RULE

This brief explanation of the Phase Rule has been purposely relegated to the last chapter, because it is felt that many students have failed to make full use of phase *diagrams* because the theoretical study of the phase *rule* does not emphasize the extreme simplicity of its practical application. The standard elementary textbooks rarely carry the phase theory beyond unary systems. Binary systems are touched upon in some cases, but ternary systems are practically ignored.

The Phase Theory deals with systems in equilibrium. A system, in this sense, is a mixture of chemical components, that is, a complex. When the mixture attains equilibrium it resolves itself into a number of phases, a **phase** being a homogeneous part of the heterogeneous system. As regards gases, these are always completely miscible and a mixture of gases is homogeneous. Thus there can only be one gaseous phase. Some liquids are immiscible, as for benzene and water, and there can therefore be more than one liquid phase. Except, however, for certain rare exceptions, aqueous solutions only give one liquid phase. With solids, however, there may be as many solid phases as there are solid chemical compounds in the system. This is assuming that solids are immiscible, which is generally the case.

The chemical entities in a mixture are called its **components** when they are independent. Chemical entities, which are dependent upon another chemical entity, are not components. For example, chlorine and sodium, of sodium chloride, are dependent upon each other. If the amount of sodium is doubled by adding sodium chloride, then the amount of chlorine is also doubled and there is only one component, sodium chloride. If, however, the system contains sodium hydroxide, hydrochloric acid, sodium chloride and water the number of components is three, since sodium chloride in this case is not a component but is dependent on the sodium hydroxide and hydrochloric acid. The two latter are components in this example because they are independent of each other. Similarly, a mixture of Glauber's salt, anhydrous sodium sulphate and water has only two components, Glauber's salt being dependent on the other two substances. In other words, the number of components in a system is the smallest number of chemical substances required to define the composition. The Phase Rule is concerned with this number and not with the nature of the components.

The *chemical* composition of a mixture may be expressed in terms of its components which do not alter in number. Its *physical* composition is defined in terms of its phases. The number of components does not vary but its phases may be altered, for example, by the physical treatment of the mixture. The total number of phases may be increased or decreased, and a phase may be made to appear or disappear.

The physical conditions to which a mixture may be subjected are temperature, pressure, electrostatic and electromagnetic fields, gravitational fields, radiant energy, etc. It is usual to ignore all these except temperature and pressure, and for condensed systems, where the effect of pressure is negligible, only one external physical condition, temperature, need be specified.

The Phase Theory is concerned with completely defining the state of a system in equilibrium. Such a definition requires a knowledge of the factors which influence the



state of equilibrium. These factors or variables are of two kinds : *external variables* and *concentration variables*, the former having been reduced to one, temperature, and the latter being the concentration of a component in a phase, expressed as mass in unit volume or as volume of unit mass. (Specific gravity or specific volume.)

The Phase Rule states that there is a relationship between the number of components, the number of phases and the number of independent variables. The independent variables are called the **degrees of freedom** : these are the number of variables which must be specified in order that the system may be completely defined without ambiguity. In order to be able to state the condition of a mixture in equilibrium it is not necessary to know all the variables. Having specified the temperature and some of the concentrations, the other concentrations can only be those required by the equilibrium, that is, they are fixed by Nature. The Rule, deduced by Gibbs, states that the number of independent variables (degrees of freedom)  $F$  is a function of the number of components  $C$  and the number of phases  $P$ .

Fundamentally, this number is  $C - P$ , being the number of independent *concentration* variables.

When temperature is introduced as a variable the number of independent variables is increased by one and the expression becomes

$$C - P + 1.$$

If pressure and temperature are introduced the expression becomes

$$C - P + 2$$

and it was in this form that Gibbs introduced the Rule.

If any of the other external variables were necessary the expression would be

$$C - P + k$$

where  $k$  is the number of external variables *which influence the system*.

The Rule is deduced from thermodynamic considerations. For a system to be in equilibrium each phase must be in equilibrium with each other phase. Consider one of the components distributed between two phases : the system will be in equilibrium when the thermodynamic potential,  $G_I$ , of the component in phase I is equal to the thermodynamic potential,  $G_{II}$ , of the same component in phase II.  $G$  is the recognized symbol for thermodynamic potential.

Suppose that an infinitely small quantity  $\partial m$  of the component passes from phase I to phase II. The *decrease* in  $G$  of the component in phase I is

$$-\frac{\partial G_I}{\partial m},$$

The *increase* in  $G$  of the same component in phase II is

$$+\frac{\partial G_{II}}{\partial m}.$$

But the thermodynamic potential must remain unchanged because the two phases are in equilibrium. That is  $\partial G = 0$ . As

$$\partial G = -\frac{\partial G_I}{\partial m} + \frac{\partial G_{II}}{\partial m} = 0,$$

then

$$\frac{\partial G_I}{\partial m} = \frac{\partial G_{II}}{\partial m}.$$

Similarly, the equilibrium of the same component between phase II and phase III may be expressed by the equation

$$\frac{\partial G_{II}}{\partial m} = \frac{\partial G_{III}}{\partial m}.$$

A third equation, that is, between phase I and phase III is redundant because of the simple law of logic that things which are equal to the same thing are equal to one another.

Thus only two equilibrium equations are necessary for three phases.

Continuing the above procedure for  $P$  phases will give  $P - 1$  equilibrium equations for the component chosen.

If there are  $C$  components there will be  $C(P - 1)$  equations. Each of these equations is dependent upon the concentration of a component in a phase and, as they are equations, they are dependent upon each other. The expression  $C(P - 1)$ , therefore, gives a figure for the number of *dependent* concentration variables.

The total number of concentration variables is found as follows. For each phase, its composition could be expressed in  $C$  terms for  $C$  components. If the composition is expressed in parts per 100 parts, then only  $(C - 1)$  terms are required. For example, if there are three components  $a$ ,  $b$ , and  $c$ , and it is known that the phase contains 10% of  $a$  and 70% of  $b$ , then it is known that the amount of  $c$  will be  $(100 - 80) = 20\%$ . In other words, although there are  $C$  terms for expressing the concentration of  $C$  components in each phase, only  $(C - 1)$  of these terms are concentration variables. As there are  $P$  phases there will be  $P(C - 1)$  concentration variables.

To this number must be added the external variables (temperature, pressure, etc.). If temperature is the only one which influences the equilibrium only one external variable is added, making  $P(C - 1) + 1$  total variables.

The number of independent variables is obtained by subtracting the number of dependent concentration variables from the above total. This gives the degrees of freedom  $F$ :

$$\begin{aligned} F &= P(C - 1) + 1 - C(P - 1) \\ &= C - P + 1 \end{aligned}$$

The more usual form in chemical literature takes pressure as well as temperature into account and so appears as

$$F = C - P + 2.$$

As regards the modified form,  $F = C - P + 1$ , this expression only applies to CONDENSED systems where temperature is the only external influence affecting equilibrium. Throughout this book it has been assumed that all the systems are condensed. This means that there is no vapour phase, but it does not necessarily eliminate pressure as a possible external variable. The reason for omitting pressure in the above deduction of the Rule is that changes of pressure have a negligible effect upon the solubility of a salt in water. Changes of pressure do, however, affect the vapour phase considerably so that it must be assumed that there is no vapour phase in order to be able to omit pressure changes. In other words, the pressure must be great enough to condense all the vapour, but the system is not necessarily isobaric. Atmospheric pressure is usually sufficient to give this condition.

It may at first appear that there must always be a vapour phase, because all aqueous solutions, and even ice, exert a vapour pressure. That this is not so will be clearly seen if the system is imagined as being enclosed in an elastic bottle. Let the system consist of water and one salt. The pressure is atmospheric, the temperature is  $20^\circ\text{C}$ . and all air has

been excluded. The bottle is completely filled by the complex with no room for vapour. If the temperature is raised, although the vapour pressure of the solution increases, no vapour phase can appear until the boiling-point of the solution is reached. Thus, systems can be considered as condensed if the temperature is below the boiling-point of the liquid phase at the given pressure.

To summarize, the phase theory shows that when the number of independent components in the system is fixed, the type of equilibrium is determined only by the number of co-existing phases. By the type of equilibrium is meant the *variability* of the system, which is expressed as the number of degrees of freedom. A system with no degree of freedom is called *invariant*. When restricting the scope to condensed systems such a system should be called "invariant condensed," but as this book is only concerned with condensed systems this term is often omitted. A system with one degree of freedom is called *univariant*, with two degrees *bivariant*, with three degrees *tervariant*, with four degrees *tetravariant*, and so on.

The number of independent components gives the *order* of the system, unary, binary, ternary, quaternary, quinary, and so on.

From the rule for condensed systems,  $F = C - P + 1$ , it is obvious that adding a component adds a degree of freedom. The disappearance of a phase has the same effect. The converse is also true.

It is now proposed to apply the rule to a few examples.

**Binary Systems** (e.g. one salt and water).

Here  $C = 2$ .

There cannot be less than one phase, and in such a case where  $P = 1$

$$F = 2 - 1 + 1 = 2.$$

Thus the maximum number of degrees of freedom is two, and the system is bivariant for a condensed system.

The minimum number of degrees of freedom is none, and when  $F = 0$ ,  $P = 3$ .

Thus the maximum number of phases possible is three.

Taking the case of **one phase** this will be unsaturated<sup>1</sup> solution. The two degrees of freedom are temperature and the concentration of the salt in the solution (or, alternatively, the concentration of the water in the solution). This means that these two must be selected to define the system. Reference to the early diagrams (e.g. Fig. 1) will illustrate that in order to fix a point within the liquid field it is necessary to know the temperature and the concentration.

When there are **two phases**,  $F = 1$  and the system is univariant. This implies that if the temperature is selected, the concentration of the solution is fixed by nature to satisfy the equilibrium. Conversely, if the concentration is selected the temperature must be the one temperature which satisfies the equilibrium. Fig. 1 was drawn on the assumption that at a fixed temperature the solubility of the salt would always be the same. This can now be considered as proved by the phase rule, so that if the temperature is known, the con-

<sup>1</sup> A saturated solution cannot be taken for the above case as a saturated solution must have a solid phase in theory. Points on saturation curves and surfaces must be considered as representing saturated solutions in contact with the solid phases. A saturated solution of one salt in water has, therefore, two phases though it is often conveniently described as all liquid. Having two phases and being of two components there is one degree of freedom. If temperature is selected the composition of the solution is fixed by nature, or if the composition of the solution is selected then only at one temperature can such a solution exist in equilibrium with the solid phase.

centration of the salt in solution is found on the saturation curve. Conversely, if the concentration of the salt in solution is selected the corresponding temperature is found on the curve.

It will be noted that, although the phase rule justifies the drawing of the curve, it does not indicate its shape or position, nor does it indicate the relative amounts of the phases. The former must be determined by direct experiment, the latter being then obtained from the diagram. Nor does the phase rule predict what the solid phase will be, it merely gives the number of phases. The composition must be determined by experiment, and the diagram can then be used to predict other points within the field. The above example assumes the solid phase to be salt. It might, of course, be ice, but the same arguments hold.

When there are **three phases**,  $F = 0$  and the system is invariant. This means that neither temperature nor concentration of the solution may be selected and the system is already defined by nature. In Fig. 1 the point *A* represents the only solution which can exist in equilibrium with both ice and salt, and the complex must be on the horizontal line through *A*.

It must be noted that defining a system is not the same thing as stating the composition and temperature of a complex. The phase rule takes no account of the relative amounts of the different phases. When a system has been defined the temperature is fixed and *the composition of each phase is fixed* (by choice or by nature), but not their relative amounts. In the bivariant case (the liquid field of Fig. 1) both temperature and composition have to be selected to mark the solution, which in this case is the complex. In the invariant case (e.g. ammonium sulphate and solution field of Fig. 1) it may appear that both temperature and composition may be selected, but this is only necessary to fix the complex. The composition of the phases is fixed by nature once the temperature has been selected.

The above argument will make clear why the solid field below the eutectic is also univariant. If temperature is selected, although the relative amounts of ice and salt may be chosen, the compositions of the ice and of the salt are fixed by nature, being pure ice in the ice phase, and pure salt in the salt phase.

When referring to selection of temperature and concentration it is obvious that such selections are always "within limits." Freedom has a limited range.

**Ternary Systems** (e.g. two salts and water).

With the addition of one more component the maximum number of degrees of freedom is increased by one, so that for a ternary system there can be three degrees of freedom.

For **one phase** the rule shows that there will be three degrees of freedom (tervariant). This must be the liquid phase, that is unsaturated solution. The three possible selections are temperature and two out of the three components for the concentration. Usually the concentration variables chosen are those for the two salts, rather than for one of the salts and water. Theoretically the three selections could be three concentrations, but in that case they would have to be expressed as mass per unit volume, which is what the phase rule really demands (see later, p. 163).

For **two phases** there will be two degrees of freedom (bivariant). Temperature may be one selection and the concentration of one of the components in one of the phases the other, or, alternatively, two concentrations may be taken. In the case where the two phases are one of the salts and a solution, it is usual to take the concentration of one of the salts in the solution phase as the concentration selection. Fig. 9 may be taken as an example. This diagram represents the whole system at 50°C., and is described as an isotherm.

The point 5 is in the field of "potassium nitrate + solution," that is, two phases and bivariant. As already stated, it should be described as "bivariant condensed." As temperature has been selected, one degree of freedom has been used up, so that the system represented by the field surrounding point 5 could be described as "univariant isothermal condensed." This leaves one degree of freedom for this field on the isotherm. Suppose the concentration of potassium nitrate in the solution phase is selected. Then nature fixes the concentration of sodium nitrate. For example, if potassium nitrate is 33%, then sodium nitrate must be 27% in the solution, giving point *y* on Fig. 9. Conversely, if the concentration of sodium nitrate were selected, then nature fixes the concentration of potassium nitrate. It will be obvious that the water concentration could have been the selection.

It should again be noted that the phase rule does not predict the concentration of the other components, it only establishes that, having selected one concentration, the other concentrations are fixed by nature. The actual figures have to be determined by experiment, and this was done before Fig. 9 could be plotted. Furthermore, having determined the composition of the solution at *y*, the phase rule does not concern itself with the composition of the complex which may contain any quantity of the solid phase in equilibrium with any quantity of the solution. This is the same as saying that the complex may be anywhere along the straight line drawn from *y* to the point representing the solid phase. Thus the phase rule has justified the use of *straight* lines as tie-lines in phase diagrams.

For **three phases**,  $F = 1$  and the system is univariant condensed. If temperature is selected the system is invariant isothermal condensed, there being only one composition of solution which is in equilibrium with two solid phases. (Point *A* of Fig. 9.) If temperature is *not* selected the concentration of one of the components might be chosen in the solution phase. In such a case temperature could only be that which nature demands to satisfy the equilibrium. Here, again, the phase rule does not concern itself with the composition of the complex, which may be anywhere within the field of solution and mixed solids.

For **four phases**, which is the maximum number,  $F = 0$  and the system is invariant condensed. There is only one solution which can be simultaneously in equilibrium with the two solid salts and with ice, and this condition can only exist at one temperature. These factors are all fixed by nature and man has no choice, unless he can find another external variable which has an influence. When ice is present pressure does have an appreciable effect, and in the deduction of the formula, if such a formula were to be used for ice, pressure should have been included making  $F = C - P + 2$ . The four-phase system then becomes univariant but, although pressure has now been introduced, the system will still be condensed unless the pressure is so reduced that a vapour phase appears.

**Quaternary Systems** (e.g. three salts and water).

For a system of four components when there is one phase, the formula shows that there are four degrees of freedom. That phase must be liquid (i.e. unsaturated solution), and there is free choice, within limits, of temperature and of the concentration of three of the components in the solution.

For two phases there are three degrees of freedom : temperature and the concentration of two of the components in the solution, or, if the concentrations of three of the components in the solution are selected, then there is no choice of temperature. A phase diagram for four components can be represented within a tetrahedron with the components situated at the four corners. Saturated solutions are represented on three surfaces within the figure forming one irregular surface, and as temperature is changed this surface moves towards

or away from the water corner. To plot a point within the tetrahedron three dimensions are necessary; these can be the concentrations of three of the components. When such a point has been plotted the saturation surface may be imagined as being moved by change of temperature. There can be only one position of the surface, and therefore only one temperature, when the point is on the surface. Thus, if three concentrations are selected, there is no choice of temperature, and the system is *tervariant condensed*. If temperature is selected there is only a choice of two concentrations and the system is still *tervariant condensed*, although it may be described as *bivariant isothermal condensed*.

When there are three phases the system becomes *bivariant*, the two degrees of freedom being temperature and one concentration, or, alternatively, two concentrations. The solution would be on one of the lines where two saturation surfaces meet, and an extension of the argument given for two phases will show that one concentration choice has been lost, since the solution lies on a line instead of a surface.

In the same way for four phases a further concentration choice is lost, and the solution in this case is represented by the point where the three surfaces meet. This system is *univariant condensed*, there being a choice of *either* temperature or one concentration.

A condensed quaternary system to be *invariant* must have five phases. These are, in their simplest form, solution, three solid salts and ice. This can only happen at one temperature and with one composition for the solution. If double salts or hydrates are formed the maximum number of phases still remains five.

In the above examples of quaternary systems only the solution has been considered. Just as in the ternary systems the complex was somewhere within the field in question, so the quaternary complexes lie within three-dimensional fields which are parts of the tetrahedron. Reference to Figs. 25, 26 and 27, which show the dissection of a pyramid, can be made to illustrate this. Although the pyramid has a square base, the system is quaternary and the arguments given hold for this figure also. Fig. 25 shows four *tervariant* systems; with the tetrahedron there are only three such systems. Fig. 26 shows four *bivariant* systems similar to the three which would be found in the tetrahedron. Fig. 27 shows two *univariant* systems at 5 and 7; in the tetrahedron there would only be one.

**The Concentration Variable.** In all the above examples it was assumed for convenience that the concentration of a component to be selected applied to the solution phase. In practice this is nearly always the case. But the phase rule allows the concentration of any component in *any* phase to be selected. The concentration of a component in a solid phase of its own composition could be selected if it be remembered that concentrations are volume concentrations expressed as mass of component per unit volume of phase. Thus the concentration of salt as a component in the same salt as solid phase, even though its composition may be 100%, may vary in concentration. This is equivalent to giving its specific gravity or specific volume which at a stated pressure is controlled by the temperature. That is, it would be substantially a temperature selection.

The concentration of a component in unit volume of another solid phase may also be selected, but if the solid is pure the selection is meaningless, being nil. If, on the other hand, there is a concentration, that is, the solid phase does contain some of the component in question, then it is obviously a case of solid solution and the selection would be feasible. This, however, is beyond the scope of this elementary work. The concentration of a component in a solid phase must not be confused with the composition of a mixture of two solid phases in a mixed field.

It may appear to the reader that, in view of the above, the general usage of weight per

weight composition (e.g. %), instead of volume concentrations, is unsound. When the diagrams are plotted on a percentage composition basis the error cancels out. The practical value of phase diagrams justifies the use of composition by weight.

The question of the phase rule allowing the choice of the concentration of any component in any phase has led to a school of thought which takes the view that no solid phases in equilibrium with solutions can be pure. In other words, solid solution is assumed to be universal, and throughout this book where a solid phase has been assumed to be 100% pure, this would not be strictly accurate. Any change in the composition of the solution, this school states, would result in a corresponding change in the composition of the solid phase, however small that change might be, so that each particular solution composition would correspond with only one solid phase composition. A. C. D. Rivett, *The Phase Rule and the Study of Heterogeneous Equilibria*, 1923, supports this school. The authors do not agree with Rivett, but one example is now given of its implication to phase diagrams.

Taking Fig. 9, the complex at 5 gives solution of composition  $y$  and solid potassium nitrate, but the latter would not be absolutely pure; it would contain a small quantity of sodium nitrate and of water and these quantities would be fixed. If the solution composition is altered the amounts of sodium nitrate and water in the potassium nitrate would also alter in the same direction. Thus the line from  $y$ , through the point 5, would stop at a point representing solid just within the potassium nitrate corner. The locus of a number of such points, representing solids, would be a curve very close to the potassium nitrate corner but not coincident with it. The line joining one solution point to its corresponding solid point is called a tie-line, and it is therefore clear that to select the concentration of a component in the solid phase is the same as selecting the concentration of the same component in the solution phase.

Although this book does not deal with solid solution, two cases have been given, Fig. 21, where the composition of the solid phase varies considerably with change of composition of solution, and in such a case the tie-lines have to be drawn on the phase diagram.

The idea of universal solid solution, as expounded by Rivett, appears to have been introduced to explain the apparent discrepancy between the theory which gave choice of any component in any phase, whereas in practice this did not appear to be true. It is no doubt true that solid phases are not pure, but the reason is more likely due to the lattice structure of matter and is no concern of the phase rule. The rule does not state that the solid phases are pure or impure.<sup>1</sup> A large number of the cases which apparently presented difficulty disappear when it is realized that concentrations are in terms of mass per unit volume as far as the theory is concerned, even though the diagrams use composition by weight.

<sup>1</sup> See p. 72 *et seq.* for further explanation.

## INDEX

This book has dealt with four systems, two-, three-, four-, and five-component, the four-component being principally the reciprocal salt pair. The main references in the index are under the terms given above, but other references, which are subdivided, use the terms binary, ternary, quaternary and quinary to indicate the kind of system with which the reference is concerned.

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